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PROCEEDINGS OF THE  
SECOND  
INTERNATIONAL CONFERENCE ON  
BITUMINOUS COAL



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VOLUME II

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# THE RATIONAL CLEANING OF COAL

By R. LESSING

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The preparation of coal for the market is mainly concerned with the removal of its ash-forming components. It may be contended that the other form of its preparation, viz., the subdivision of coal into various sizes by screening, is of a greater actual importance, inasmuch as a larger tonnage of coal is submitted to this treatment than to cleaning operations. It must however be remembered that the question of size is not unconnected with that of ash content.

The preference of the coal buyer for large or "round" coal has its origin in the fact that its size is an implied guarantee of its purity, or at any rate of its freedom from those mineral constituents which form lines of weakness along which coal is broken during mining, handling and transport.

The original methods of firing coal both for domestic and industrial uses were based on the cheap supply of such large and therefore comparatively clean coal. The tendency during the present century has been in the direction of utilizing coal of smaller size, a tendency which has been pressed to its logical conclusion in the application of coal in dust form, and most remarkable and greatly improved combustion efficiencies are now realized. It so happens that this tendency coincides with the modern development of coal mining, which of necessity has to deal with poorer seams and yields more small coal on account of blasting and machine cutting.

It is not yet sufficiently realized, either by the coal producer or the consumer, that such small coal possesses the advantage of containing in the slack or duff sizes a very clean and ash-free coal, and that the free dirt particles, which impart to the slack or duff their high mean ash content, are present merely in mechanical admixture.

The methodical examination of the distribution of mineral matter in coal is of comparatively recent date. Until a few years ago coal cleaning was carried on without sufficient consideration for the true composition of the coal and the distribution and chemical composition of its ash-forming constituents. The author showed in 1920 that

the ash in the main constituents of banded bituminous coal, fusain, vitrain, clarain and durain is of an amount and a composition characteristic for each component<sup>1</sup> and further<sup>2</sup> that the distribution of mineral matter throughout its components varies both in quantity and composition according to the size of particle. It may be said that this recognition forms the key to new work, revealing new facts and establishing old ones on a sound scientific bases.

The results and their significance were discussed in a number of papers which should be referred to in the original publications.<sup>3-13</sup>

I had the privilege of presenting a survey of these investigations in my contribution<sup>9</sup> to the First International Conference on Bituminous Coal in 1926, in which the possibility of refining the natural product and of concentrating its intrinsic value, was foreshadowed.

The principal outcome of these researches was that clarain and vitrain, the "bright" coal constituents, have an ash content not exceeding 1.5 or 2 per cent, of a chemical composition which makes it tolerably certain that this ash forms the remains of the original plant ash. Durain, the "dull" coal constituent, has a higher ash content, which is composed of almost pure clay substance. It represents the argillaceous mud, intermingled and deposited with comminuted plant

<sup>1</sup> "The Mineral Constituents of Banded Bituminous Coal." Trans. Chem. Soc., 1920, 117, 256.

<sup>2</sup> "Studies in the Distribution of Mineral Matter in Coal." Trans. Inst. Min. Eng., 1921, 60, 288.

<sup>3</sup> "The Study of Mineral Matter in Coal." Fuel, 1922, 1, 6.

<sup>4</sup> "The Disintegration of Coal by Acids." Trans. Inst. Min. Eng., 1923, 64, 296.

<sup>5</sup> "The Influence of Catalysts on Carbonization." Trans. Chem. Soc., 1924, 125, 2344.

<sup>6</sup> "The Inorganic Constituents of Coal." J. Soc. Chem. Ind., 1925, 44, 277T.

<sup>7</sup> "The Influence of Ash Constituents on the Coking Process." J. Soc. Chem. Ind., 1925, 44, 345T.

<sup>8</sup> "Coal Ash and Clean Coal." Roy Soc. Arts, Cantor Lectures, 1925; Fuel, 1926, 5, 17, 69, 117.

<sup>9</sup> "Coal and Its Mineral Matter." Proc. Int. Conf. on Bituminous Coal. Pittsburgh, November, 1926, 165.

<sup>10</sup> "Steenkohlen en hun Minerale Bestanddeelen." Polytechnisch Weekblad, 1927, 21, 533.

<sup>11</sup> "Die Mineralbestandteile der Steinkohle." Z. Oberschles. Berg-& Huettenm. Ver., 1928, IV.

<sup>12</sup> "Clean Coal in the Coking Industry." Gas World, Coking Section, May, 1928, 14.

<sup>13</sup> "Les Fondements du Nettoyage du Charbon." 2. Congrès du Chauffage Industriel, 1928.

particles or small plant entities such as spores, etc., which is intimately mixed with the coal substance and gives durain its characteristic hardness. On account of its close and uniform association with the coal substance, the ash of durain cannot be removed by ordinary washing or cleaning processes, and must be regarded as inherent ash.

Fusain, the peculiar charcoal-like constituent of bituminous coal, is quite different from the other coal constituents, in the composition of both its carbonaceous and its mineral matter. The latter consists mainly of the suspended and dissolved solids deposited from water

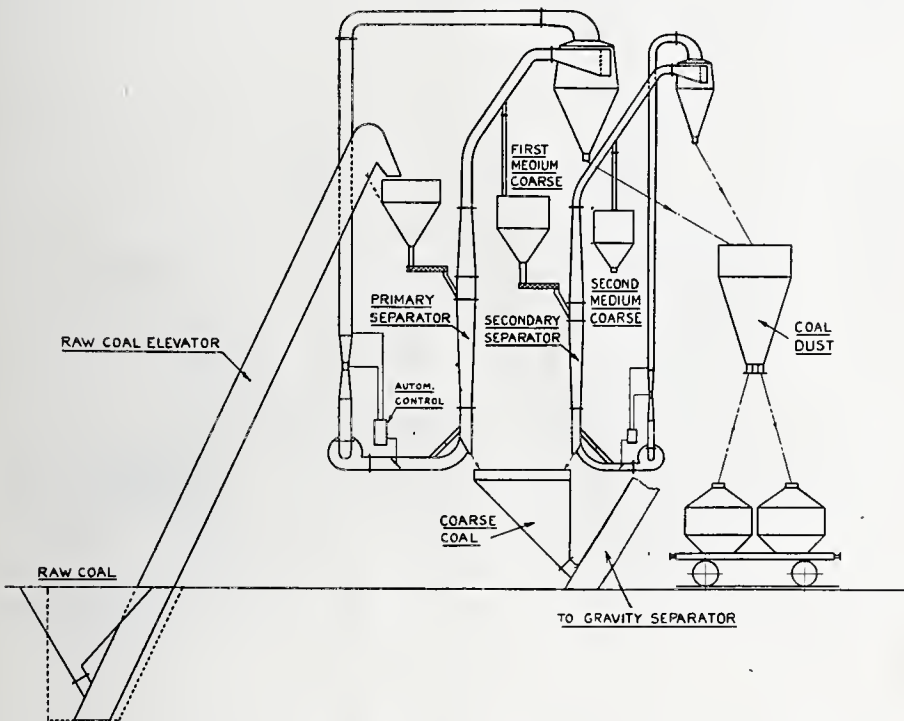


FIG. 1. DIAGRAMMATIC ARRANGEMENT OF DE-DUSTING PLANT

which percolated the fusain intrusions during and after fusainization by infiltration into the coal seam. This mineral matter consists therefore largely of the carbonates of lime and iron, together with a small amount of clayey matter, originally suspended in the percolating water.

The fusain, by reason of its friability, is almost entirely in the form of dust in the coal brought to the surface, except for portions which remain occluded in unbroken lumps of coal. This dust is mixed up with the dust formed by the more friable portions of the clarain and

durain, together with the dust of shale and other minerals. It presents its own peculiar problems in cleaning operations, and is responsible for the formation of slurry in wet washing and of dust in dry cleaning processes, introducing in both cases considerable difficulties in handling and recovery, and interfering with the production of a clean coal of good appearance and low ash content. The presence of this dust is responsible for difficulties in draining the excess water off the washed coal and makes the preparation of a product of a reasonably low free moisture content impossible. Recently, these difficulties have led to the screening out of dust from slack to be washed, but in order to make screening practicable, a fair amount of clean coal above true



FIG. 2. COAL DUST WAGON

dust size is allowed to pass the screen, whilst rather high percentages of dust still remain in the coarse mixture to be submitted to washing. On the Continent, pneumatic removal of dust has been practiced of late, but a close "cut" between true dust and the larger particles of small coal has not been attempted.

Coal washing processes with few exceptions depend on the separation of the specifically lighter coal from the heavier dirt in a current of water. This is done either in a continuous current of water as in trough washers or in pulsating bodies of water as in jig washers and on concentrating tables.

The difficulty of draining the washed coal to a reasonable free moisture content has led to the adaptation for the dry cleaning of coal of

pneumatic cleaning processes, such as had been employed for other materials, particularly grain, flour, coffee, etc.

Except in the special processes referred to, in which the difference in specific surface properties of coal and refuse, such as friction or wetting power are made use of, the separation of coal and free dirt depends both in wet and dry cleaning on at least two factors, specific gravity and size, by which the rate of bodies falling or rising in such media as water or air, both lighter than the material, are determined.

According to the laws governing the phenomena involved, a large particle of clean coal and a small particle of refuse, say for instance in a size ratio of 5 to 1, would travel in water in the same direction and practically at the same velocity.

The two particles, although discrete and free to move away from each other would not part company but would find their way together either into the "clean" coal product or into the refuse. In consequence a sharp separation is impossible and a certain amount of dirt will always be present in the coal and some coal in the refuse.

A good deal of mathematical evidence has been adduced in explanation of the phenomena involved and the formula enunciated by Rittinger and Stokes' law of bodies falling in water are freely used in their theoretical consideration. As these laws only hold good for true spheres and require certain constants to render them applicable to cubes or other shapes, their value is considerably diminished when the difference in shape of clean coal particles and shale particles assert themselves, and still more when, as in the case of fusain, the porosity of the particles introduces difficulties on account of adsorbed air which affects the buoyancy of the particle.

The dependence of ordinary washing and dry cleaning processes upon two factors is responsible for the comparative inefficiency of such processes in regard to the production of truly clean coal with a minimum of loss. Whilst experience has made it possible for such old established washing plants as the jig washer to dispense with a complicated system of grading, sizing within very close limits is still necessary in most successful dry cleaning processes, but it may be confidently stated that in no existing commercial process can a coal containing only inherent ash be produced without considerable loss of such coal in the refuse portion.

These considerations led the author to investigate some years ago the possibilities of devising a commercial method depending on a single factor as the separating criterion. The most attractive line of

investigation appeared to be a separation by specific gravity only. The difference in specific gravity of coal and shale has been used in the laboratory for many years for the differentiation between these two materials by the so-called float-and-sink test. This method is now widely used for the control of washeries and for the examination of coal before and after washing. By submitting a coal to the float-and-sink test at different specific gravities, washability curves can be constructed which demonstrate the yield of products and their ash content theoretically obtainable at any given density of the separating fluid. The fluids used are either aqueous solutions of inorganic salts,

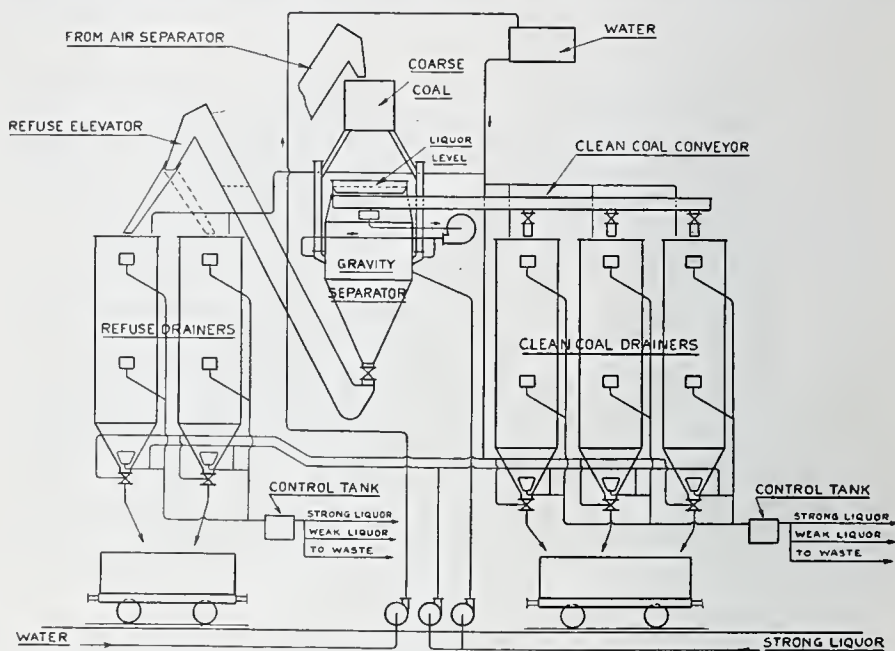


FIG. 3. DIAGRAMMATIC ARRANGEMENT OF GRAVITY SEPARATION

such as calcium chloride, zinc chloride and others, or organic liquids such as mixtures of carbon tetrachloride and petroleum ether as suggested by the author.<sup>14</sup>

### COMMERCIAL GRAVITY SEPARATION

The application of the float-and-sink method on an industrial scale presented some formidable difficulties; problems of the complete removal of the density liquid from the coal, its quantitative recovery after use and its likely corrosive action upon the plant were antici-

<sup>14</sup> "Studies in the Distribution of Mineral Matter in Coal." Trans. Inst. Min. Eng., 1921, 60, 288.

pated. The fascinating possibility of being able to separate all cleanable coal from raw coal regardless of size, so that it would contain a minimum of ash, was a sufficient inducement to devote a very great amount of research and experimental work to the subject.

After the preliminary work in the laboratory, the Clean Coal Company, Ltd., took up this investigation, and a semi-commercial plant capable of treating about 2 tons of coal per hour, has been in operation during the last three years. This unit has been used for the collection

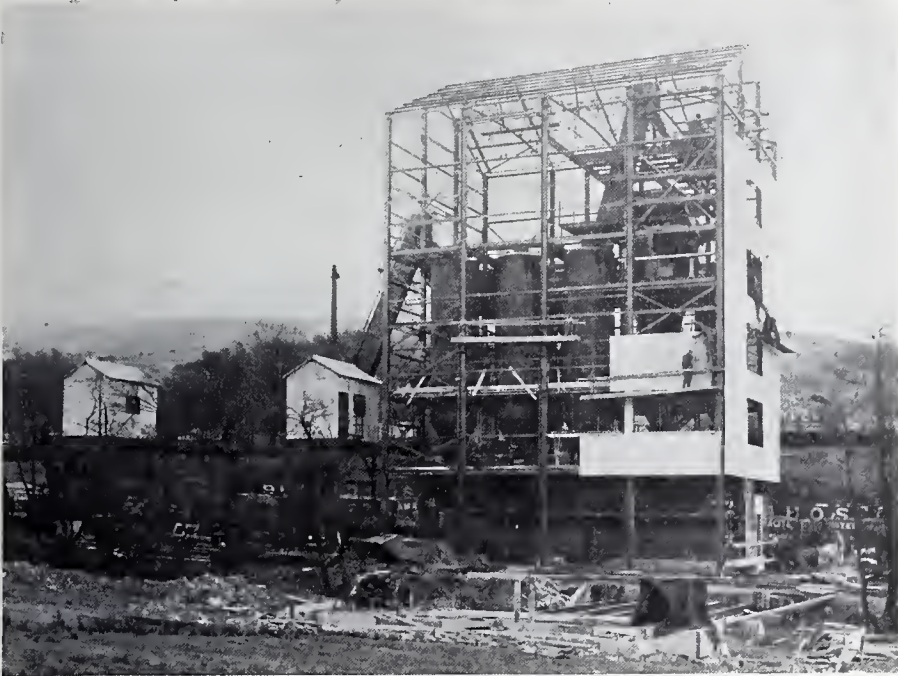


FIG. 4. CLEAN COAL PLANT AT YNISCLEDWYN COLLIERY, DURING ERECTION.  
FROM THE WEST

of data, upon which the design of commercial plants has been based, and for the examination of coal in 10- or 20-ton lots.

The first commercial unit (Figs. 4, 5 and 6) was erected at the Yniscledwyn Colliery of Messrs. Amalgamated Anthracite Collieries, Ltd., and has been in operation for some time, dealing with 20 tons per hour of anthracite duff of a size  $\frac{3}{16}$  inch to 0.

#### PRINCIPLES OF THE PROCESS

The characteristic properties of the fusain and other coal dust indicated that its removal before gravity separation would be desirable

and steps were taken right from the beginning to effect the de-dusting of the coal to be treated. It was, however, not foreseen how thorough this de-dusting had to be, in order to make ready drainage of a somewhat viscous density liquid possible. Preliminary experiments had shown that all dust below  $\frac{1}{100}$  inch (50 I.M.M. mesh) should be removed. To begin with, a content of 5 per cent of such dust in the coarse coal was fixed as a permissible limit. It was, however, soon found that the coarse coal had to be much more free of dust in order to

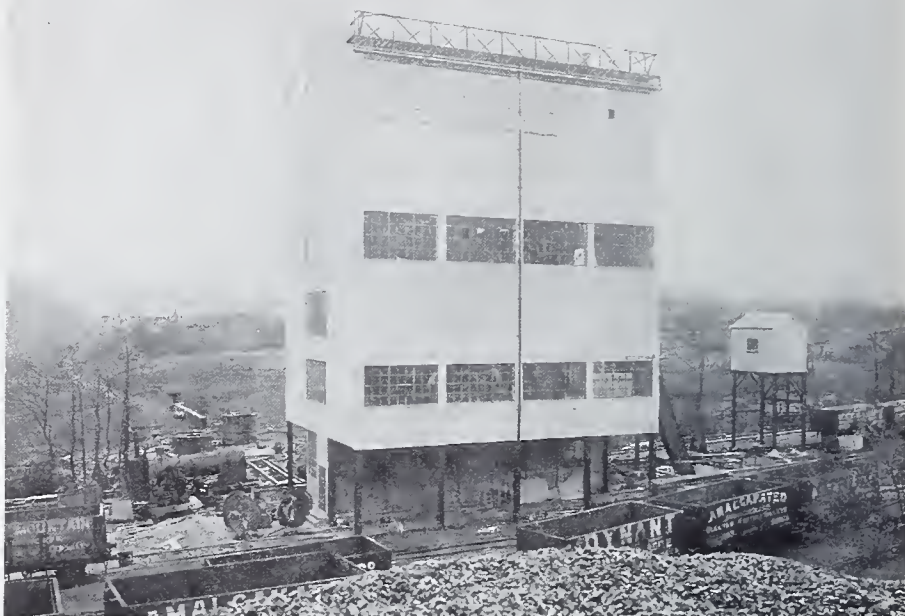


FIG. 5. CLEAN COAL PLANT AT YNISCEDWYN COLLIERY, DURING ERECTION.  
FROM THE EAST

give good draining results, and it is now considered desirable to keep the dust content down to 0.5 or 0.25 per cent.

The dust recovered is, for the reasons given above, not amenable to cleaning and as it is of a size directly utilizable in powdered fuel installations, its obvious use lies in that direction.

In this connection it must be remembered that in Great Britain 10 to 20 million tons per annum of such natural dust are raised with the coal and only require separation and collection to be ready for coal dust firing without further grinding or other preparation.

The gravity separation of the de-dusted coal calls for little comment.

Inasmuch as this separation is carried out on the de-dusted material, it is scientifically much more accurate than the ordinary laboratory float-and-sink test carried out on raw coal without dust removal. For it should be remembered that the great majority of float-and-sink tests are vitiated by contamination with this dust, the bulk of which is not amenable to gravity separation.

Ordinarily a calcium chloride solution of suitable specific gravity is used as the separating fluid, but it can be replaced wholly or in part by other liquids when it is desired to modify the density, viscosity or other properties.

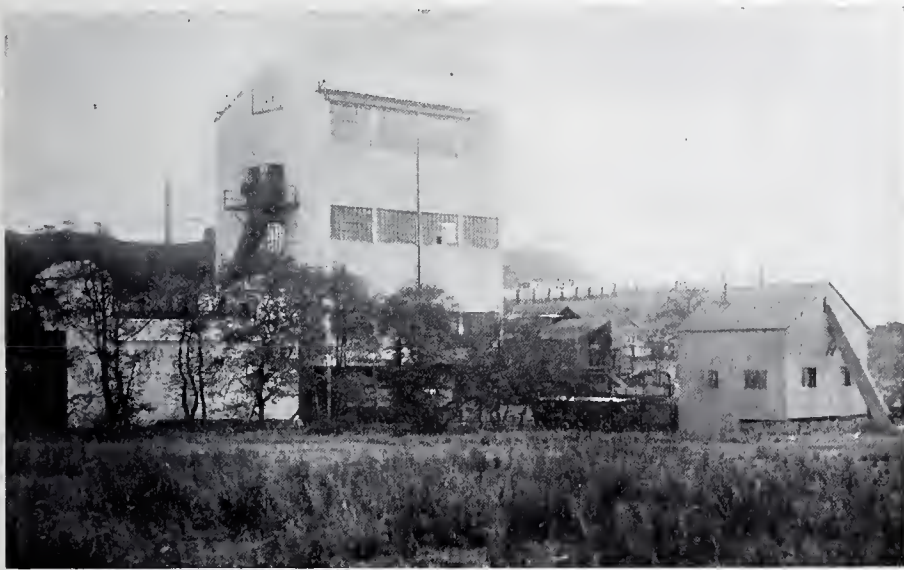


FIG. 6. YNISCEDWYN PLANT COMPLETED. FROM THE NORTH-WEST

From the commercial point of view the crux of the process is the removal of the calcium chloride solution from the coal and refuse and its recovery in a form suitable for recirculation through the process.

The removal of even the last traces of calcium chloride from the product does not any longer present difficulties, in fact it is our usual experience that coal which naturally contains chloride gives a considerably lower chloride test after having passed through the process than before, the original salt being washed out along with the calcium chloride.

The clean coal and refuse suspended in the solution are placed in draining hoppers; the solution is allowed to run off, whilst water is superimposed upon it, so that a very methodical washing takes place.

The bulk of the solution is recovered in its original strength whilst a very small layer of weak liquor is interposed between the strong liquor at the bottom and the clean water at the top. This weak liquor is passed through an evaporator before being put again into circulation. A small portion of solution, so dilute that it does not stand the cost of concentration is run to waste until water free from added chloride passes out. The calcium chloride lost in this manner usually amounts to no more than the equivalent of about  $\frac{1}{2}$  gallon of strong calcium chloride liquor per ton of coal.

#### DESCRIPTION OF PLANT

The plant consists of three main sections:—the removal of dust by air separation, the gravity separation and the re-concentration of liquor.

1. *Air separation.* When this work was begun, a number of existing types of air separators were tried, with little success. They were not able to treat a sufficient tonnage to comply with the requirements of ordinary commercial coal cleaning plants, nor did they even approach the limit set for the degree of freedom of dust of the coarse coal or for the fineness of the dust capable of immediate use in coal dust burners.

A new type of air separator was therefore worked out and submitted to extensive trials. It is shown in diagrammatic form in Figure 1. Its advantages are: a closed system free from external dust troubles, a sharp cut between dust and coarse coal, small ground space required and low power for running. The apparatus is designed to give the correct velocity of air at every point of the system and is automatically controlled to compensate for variations in the coal feed and the speed of fan.

In order to allow for the production of a coarse product as free as possible from dust, and at the same time to produce fines having the correct screen analysis for coal dust firing, a portion or portions of medium size are taken out of the primary system of the air separator and retreated in a secondary unit of suitable dimensions, where a final separation into coarse and fines takes place.

The fines produced are either pumped directly to coal dust fired colliery boilers or else are loaded into special coal dust wagons for transport to customers' installations where they are discharged by means of compressed air. A type of coal dust wagon introduced by the Clean Coal Company which is believed to be the first specially designed for British Railways, is shown in Figure 2.

*2. Gravity separation.* A diagram of this portion of the plant is shown in Figure 3. The dust-free coal is elevated into a bunker over the gravity separator, into which it is fed through two or more chutes and feeder tubes. Where dust-free nuts are to be cleaned, these may be charged into the gravity separator together with the dust-free slack or duff, or else they may be treated in another unit.

The separating vessel consists of a cylindrical vessel with a conical base and a rectangular top, the size being determined in accordance with the throughput required. The raw coal is introduced through the sides of the vessel by means of feeder tubes, provision being made for the rapid detachment of the particles from each other and their distribution across the separator.

The rate of feed of the coal is controllable, but it may be pointed out that the efficiency of the separation does not depend on a uniform feed as is the case with all other processes.

The particles of coal of low ash content immediately rise in the separating liquor to the top of the vessel and are skimmed off continuously by means of a conveyor of the scraper type, and transferred together with any excess of liquor into a screw conveyor which delivers the clean coal and liquor into one of three or four draining hoppers. Some of the liquor used for feeding the raw coal overflows through a grid at the top of the vessel and is recirculated by means of a centrifugal pump. The excess liquor which overflows and passes to the drainers with the clean coal, is replaced by fresh calcium chloride liquor drawn from a stock tank.

The refuse sinks to the bottom of the separator and passes into the boot of an elevator mounted in a liquor-tight casing. This elevator delivers the refuse into one of two drainers similar to those used for draining the clean coal.

The clean coal and refuse drainers consist of cylindrical vessels with conical bases of a total height of approximately 30 feet, the diameter being from 6 to 9 feet according to the throughput of the installation. The bottom portion of the cone is provided with a valve which is so designed that, whilst being liquor-tight when closed, it permits of rapid and controllable discharge of the drained coal. The cone is also equipped with boxes containing grids through which the liquor is drained off. Owing to the previous removal of the dust from the coal, draining takes place at a very rapid rate, and the bulk of the liquor is drained off at its original strength and passed by way of a float control tank to the strong liquor stock tank. While strong

liquor is being withdrawn at the bottom of the drainer, fresh water is sprayed on at the top of the drainer in such a manner as to avoid dilution of the liquor. As the strong liquor level falls in the drainer, the super-imposed water washes the particles of coal free from calcium chloride solution, and in its passage down the drainer forms a comparatively shallow layer of weak liquor, the specific gravity of which varies from, say 1.4 at the bottom of the layer to 1.0 at its top. Sufficient water is added in this way to wash the coal or refuse entirely free from chloride and allow a slight excess of chloride-free water. Immediately the diluted portion of the liquor reaches the float control tank, one float sinks, operating an electric signal, whereupon the operator diverts the outgoing solution into a weak liquor main and thence into the weak liquor stock tank. The specific gravity of the solution falls very sharply, and at a predetermined point a second float in the control tank sinks, operating another signal, when the remaining liquid, which contains a very small and negligible quantity of calcium chloride, is passed down the waste pipe. The equivalent of strong liquor lost in this way amounts to less than half a gallon per ton of raw coal. The amount of fresh water required in washing varies somewhat with the nature and size of coal treated, but it may be taken as being of the order of 120 gallons per ton of raw coal. If desired, most of this water can be collected and reused.

Owing to the close "cut" obtained in the air separator and the complete removal of dust from the coal, the washing and draining process is rapidly effected and occupies only about  $1\frac{1}{2}$  hours for each drainer. At the end of this period, when the washing water has ceased running, the drainer is discharged either into wagons or upon a conveyer by opening the bottom valve a few inches. The free moisture content of the coal is so quickly reduced to below 5 per cent that even small coal, passing say a  $\frac{1}{4}$ - or  $\frac{3}{16}$ -inch screen, runs easily out of the drainer. Where trimming of wagons permits it, a drainer can be discharged in 10 minutes.

*3. Concentration of weak liquor.* Weak liquor is formed at a rate of about 70 gallons per ton of raw coal, its average specific gravity being approximately 1.2. This liquor is passed through a simple tubular steam-heated evaporator to raise its specific gravity to 1.4, and the concentrated solution is returned to the strong liquor tanks for further use.

By a special treatment the liquor is rendered entirely non-corrosive to iron and steel, and the semi-commercial plant in which it has been used for three years has remained entirely free from corrosion troubles.

At the Ynisedwyn Plant steam is raised with washery refuse containing an average of about 60 per cent of ash. Although the author entertains strong views on the advantages of employing coal with a minimum ash content for most purposes, the utilization of fuel of the lowest grade is justifiable provided the transport and handling charges are also kept below the economic limit and this can only be done at the colliery.

### CLEANING RESULTS

The results obtained from the treatment of a number of coals tested in the semi-commercial plant in quantities of 10 to 20 tons are recorded in Table I. In explanation it should be stated that these coals were treated without the opportunity of ascertaining the best conditions in each case and it is therefore to be expected that with a little experience with the behavior of each individual sample in the air and gravity separation the results would be better.

The "fines" have a screen analysis which permits their direct employment for dust firing. The "fines" obtained commercially from anthracite duff in the Ynisedwyn plant are now satisfactorily burned in several installations without any adjustment of the existing powdered fuel burners. It is therefore tolerably certain that those produced from bituminous coal can also be burned without any difficulty.

This indicates the possibility of an enormous expansion of coal dust firing. I estimate that the natural coal dust available in Great Britain is of the order of 10 to 20 million tons per annum which by the simple expedient of air separation can be put on the market, ready for the burner without further grinding. The provision of grinding mills can therefore be dispensed with and the most costly and troublesome portion of present-day coal dust firing equipment becomes obsolete. Incidentally the controversy between the adherents of the central and the unit system of grinding will be settled by the disappearance of both.

The production of a "medium coarse" product calls for some comment. The yield of this fraction need not exceed 5 per cent of the raw coal in the case of smalls and will be less in the case of the larger sizes. The figures shown in brackets in Table I represent yields from one air separator only, as a secondary separator is not provided in the semi-commercial plant. This fraction is not a middlings product in the ordinary sense, i.e., one of a medium high ash content, but it represents a mixture of sizes which must be withdrawn in order to

TABLE I

SCREEN SIZE	DURHAM COKING COAL				COKING		STEAM COALS				ANTHRACITE
	Trebles	Doubles	Singles	Small	Welsh	Yorkshire	Durham	Durham	Nor-thumberland	Welsh	Duff
	3½"-1½"	1½"-1"	1"-¾"	¾"-0	½"-0	1"-0	½"-0	1"-0	1"-0	3"-0	¾"-0
<i>Yields of products (air-dry basis):</i>											
Fines.....	—	—	—	13.4	7.1	5.2	3.9	1.6	4.5	8.1	12.5%
Medium coarse.....	—	—	—	(10.2)*	—	(9.6)*	(10.1)*	(1.5)*	(7.4)*	—	(5.4%)*
Clean coal.....	74.5	65.2	75.7	61.6	77.2	71.8	72.2	81.4	65.5	59.0	58.7%*
Refuse.....	25.5	34.8	24.3	14.8	15.7	13.4	13.8	15.5	22.6	32.9	23.4%*
Total products.....	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0%*
<i>Ash in products:</i>											
Fines.....	—	—	—	15.04	11.65	10.14	14.05	12.36	22.65	13.95	12.85%
Medium coarse.....	—	—	—	15.23	—	18.38	15.09	9.22	26.90	—	11.10%
Clean coal.....	5.02	4.40	3.65	3.25	3.28	1.04	3.49	2.90	3.00	1.54	1.28%
Refuse.....	54.14	62.54	58.99	62.00	56.84	69.94	53.45	62.00	60.10	67.00	56.20%
Original sample.....			17.36	14.82	12.21	14.58	11.85	12.86	22.32	25.30	16.30%
<i>Ash contributed to entire sample:</i>											
Fines.....	—	—	—	2.0	0.8	0.5	0.6	0.2	1.1	1.0	1.6%
Medium coarse.....	—	—	—	1.6	—	1.8	1.5	0.1	2.0	—	0.6%
Clean coal.....	3.7	2.9	2.8	2.0	2.5	0.8	2.5	2.4	1.9	0.9	0.8%
Refuse.....	13.8	21.8	14.3	9.2	8.8	9.4	7.5	9.7	13.6	22.1	13.1%
Total products.....	17.5	24.7	17.1	14.8	12.1	12.5	12.1	12.4	18.6	24.0	16.1%
Original sample.....			17.36	14.82	12.21	14.6	11.8	12.9	22.3	25.30	16.30%

<i>Calorific value:</i>									
Fines.....	—	—	12,430	13,280	13,250	12,510	13,040	9,530	12,850 B.t.u./lb.
Medium coarse.....	—	—	12,230	—	—	—	—	—	13,560 B.t.u./lb.
Clean coal.....	14,310	14,480	14,680	14,860	14,630	14,250	14,280	12,950	14,900 B.t.u./lb.
Refuse.....	—	—	3,890	5,240	—	—	—	3,390	5,710 B.t.u./lb.
Original sample.....	—	—	12,580	12,850	—	12,420	—	10,310	12,020 B.t.u./lb.
<i>Volatile matter (less moisture):</i>									
Fines.....	—	—	27.08	22.29	22.78	25.22	27.98	21.18	6.68%
Medium coarse.....	—	—	29.26	—	29.93	29.57	31.89	30.08	6.12%
Clean coal.....	30.39	30.82	31.91	27.82	35.78	33.44	34.73	35.88	6.00%
Refuse.....	17.99	16.84	18.08	14.71	20.52	22.90	16.52	22.73	4.75%
Original sample.....	27.21	28.73	29.18	24.88	30.80	31.30	32.46	30.44	5.90%
<i>Sulphur:</i>									
Fines.....	—	—	1.39	0.84	0.77	1.81	1.43	1.96	1.08%
Medium coarse.....	—	—	1.77	—	—	—	—	—	1.14%
Clean coal.....	0.42	1.04	1.08	0.73	0.90	1.49	0.73	0.97	0.70%
Refuse.....	—	—	1.83	0.48	—	—	—	1.23	2.49%
Original sample.....	—	—	1.20	0.75	—	2.29	—	—	1.18%
<i>Chloride in terms of Cl:</i>									
Fines.....	—	—	0.064	—	0.518	0.010	0.024	—	—
Clean coal.....	—	—	0.012	—	0.028	0.007	0.007	—	—
Original sample.....	—	—	0.021	—	0.177	0.014	0.004	—	—

\* Not treated in secondary air separator.

comply with the specification of screen sizes in the "fines" and "coarse" portion. It is simplest dealt with by returning it to the raw coal feed, when it will yield further quantities of "fines" and "coarse;" in some cases it may be preferable to grind it and add it to the "fines."

The ratio of products to each other depends, of course, on the nature of each coal and varies from case to case. It can be varied within certain limits by the adjustment of the process. The efficiency of the gravity separation of the "coarse" raw coal coincides very closely with the optimum point shown by the washability curve of each coal.

With most coals the nut sizes have an ash percentage above that of the inherent ash, inasmuch as they occlude a certain amount of free dirt within their mass. In order to obtain the cleanest product, the larger sizes would have to be crushed, for the detachment and separation of fusain and "free" dirt. The gravity separation being entirely independent of size, the process is equally applicable to large and small coal and it suggests the possibility of dispensing with hand-picking of coal altogether.

The fear that coal treated in a bath of calcium chloride might not be readily freed of either chloride or moisture, is dispelled by the actual working results. The chloride is removed so thoroughly that in most cases the actual chloride content of the clean coal is lower than that of the raw coal. The question of hygroscopicity of the coal from that source does therefore not arise.

The free moisture is reduced to a very small percentage in 2 hours or less, even with the smallest duff sizes, largely on account of the pre-treatment of the coal which provides the conditions for ready drainage.

A consideration of the general physical and chemical properties of the clean coal and the coal dust produced by this process is a subject too large to be included within the compass of this paper.

Coke made from coal cleaned by this process is of particularly high quality, and as was to be expected contains a very small percentage of breeze and ballast. In one case a slack washed in an ordinary jig washer and giving a yield of 12.5 per cent breeze and ballast, yielded under 3 per cent after treatment by the process described.

The advantage of a low ash percentage in coal to be carbonized in coke ovens, gas retorts or low temperature carbonizing plant requires no further emphasis. It can be safely asserted that the possibility of producing semicoke from coals thus treated will give a

considerable impetus to the development of low temperature carbonization.

An interesting result is the reduction of the arsenic content of anthracite which is of importance for its use as fuel in hop and malt kilns. The arsenic content of two samples of anthracite, sold as specially selected for hop drying purposes, was estimated. Portions of the samples were submitted to the gravity separation process and the following results were obtained:

	<i>No. 1</i> <i>parts</i> <i>per million</i>	<i>No. 2</i> <i>parts</i> <i>per million</i>
As <sub>2</sub> O <sub>3</sub> in original sample.....	15.0	12.0
As <sub>2</sub> O <sub>3</sub> in clean coal.....	1.5	2.0
As <sub>2</sub> O <sub>3</sub> in refuse.....	40.0	50.0

The corresponding figures for the clean coal produced in the semi-commercial plant and in large scale colliery working are:

	<i>Semi-commercial</i> <i>plant.</i> <i>parts</i> <i>per million</i>	<i>Colliery</i> <i>parts</i> <i>per million</i>
As <sub>2</sub> O <sub>3</sub> in clean coal.....	1.5	1.3

### THE VALUE OF CLEAN COAL

While the study of the mineral impurities in coal was sorely neglected until about 10 years ago, their investigation is now receiving attention to an increasing extent. Their influence on the combustion and carbonization of coal is being examined and the differences in the chemical composition of the inherent ash of the various coal components and that of extraneous mineral matter has been established for many varieties of coal.

Much has been written on the value of cleaned coal, by which hitherto was understood a coal from which the major portion of mineral matter had been removed, but which still contained a considerable quantity of ash-forming matter, over and above its "inherent" ash percentage.

We have now a means by which truly clean coal can be produced commercially at a cost comparing favorably with that of the less ambitious washing processes. It might therefore be instructive to give at least one example showing the influence of the degree of purification upon an important branch of the utilization of coal, viz., its carbonization and use of the resultant coke in blast furnaces.

TABLE II

	OLD WASHERY				MODERN WASHERY				"CLEAN COAL" PLANT			
	Products		Ash		Products		Ash		Products		Ash	
	Per cent	Tons	Per cent	Tons	Per cent	Tons	Per cent	Tons	Per cent	Tons	Per cent	Tons
Clean coal.....	84.3	25,790	9.5	2,450	76.2	23,500	6.7	1,580	63.4	20,560	3.2	660
Medium coarse.....	—	—	—	—	—	—	—	—	4.9	1,590	15.2	240
Fines.....	—	—	—	—	—	—	—	—	16.0	5,200	15.0	780
Screenings.....	—	—	—	—	10.0	3,080	15.0	460	—	—	—	—
Slurry.....	2.0	610	15.0	90	—	—	—	—	—	—	—	—
Refuse.....	13.7	4,200	48.0	2,020	13.8	4,260	60.0	2,560	15.7	5,090	62.0	3,150
Total slack.....	100.0	30,600	14.9	4,560	100.0	30,840	14.9	4,600	100.0	32,440	14.9	4,830
Large coke.....	90.0	15,800	13.8	2,170	92.0	14,490	9.7	1,410	97.2	13,190	4.8	620
Breeze.....	3.0	510	13.6	70	2.0	310	12.0	40	1.1	150	6.3	10
Ballast.....	7.0	1,230	17.3	210	6.0	950	14.0	130	1.7	230	12.4	30
Total coke.....	100.0	17,540	14.0	2,450	100.0	15,750	10.0	1,580	100.0	13,570	4.9	60
	Cwt. per ton of pig iron	Tons	Cwt. per ton of pig iron	Tons	Cwt. per ton of pig iron	Tons	Cwt. per ton of pig iron	Tons	Cwt. per ton of pig iron	Tons	Cwt. per ton of pig iron	Tons
Iron melted by large coke.....	23.50	13,446	21.51	13,446	21.51	13,446	21.51	13,446	19.62	13,446	19.62	13,446
Large coke required.....	4.41	15,800	2.92	14,490	2.92	14,490	2.92	14,490	1.61	13,190	1.61	13,190
Limestone required by ash and sulphur in coke.....	6.00	2,962	3.96	1,970	3.96	1,970	3.96	1,970	2.04	1,081	2.04	1,081
Slag from coke.....		4,034		2,664		2,664		2,664		1,372		1,372

Varying figures have been given recently for the saving in the production of pig iron effected by the removal of ash from the coal before coking. The present example is based on an actual case in which colliery, coke ovens and blast furnaces are owned by the same undertaking. For the purpose of the calculations the question of purchase, sale or transfer prices of the bulk of materials and products can therefore be eliminated and the comparison of different cleaning systems is simplified by its restriction to their differences.

The calculations are based on the actual output of pig iron during one month. In Tables II and III are compared the results from an existing washery with those obtainable by the process here described. As the existing "old washery" is of an obsolescent type and design, the comparison would not be fair and the case of a "modern washery," of what is considered high efficiency, has been added.

The weights and percentages are based on actual working data and analyses, and the money values upon the commercial information supplied by the firm.

The comparison of materials given in Table II shows the quantity of raw slack required in each case to give the necessary amount of "clean" coal which will produce the coke required for the given output of pig iron. The coke requirements per ton of pig vary with the content and composition of the coke ash. The yields of large coke, breeze and ballast from the three "clean" coals vary according to the ash content of the clean coal, whilst the products from the cleaning plants vary according to the process employed.

The money values of the differences between the materials required and the products made with the aid of the "modern" washery or the "clean coal" plant on the one hand, and the corresponding figures for the "old" washery on the other, are given in Table III. This detailed comparison between the three coals containing 9.5, 6.7 and 3.2 per cent ash respectively in their influence upon the economics of the blast furnace shows the ascertainable saving from coal to pig iron to be of the order of 2/6d. per ton of pig for approximately every 3 per cent of ash reduction. The figures do not include the saving derived from the faster driving of the blast furnace nor the increment in value due to the higher quality of iron produced.

The results of these calculations do not bear out the opinion sometimes expressed, that cleaning of coal below a certain reducible ash content does not offer corresponding advantages; on the contrary, it emphasizes the practical importance of preparing coal containing no more than the inherent ash which cannot be removed mechanically.

TABLE III  
COMPARISON WITH "OLD WASHERY"

DEBIT				CREDIT			
	Modern washery		"Clean coal" plant		Modern washery		"Clean coal" plant
	Tons per month	£	Tons per month £		Tons per month	£	Tons per month £
Extra raw slack required @ 6/-	240	£72	1,840	Medium coarse @ 6/-	—	—	1,590
Disposal of extra refuse @ -/6.	60	2	900	Fines @ 8/6	—	—	5,200
Difference in value of breeze and ballast @ 8/-	480	192	1,360	Screenings @ 7/-	3,080	£1,078	—
Balance representing saving in pig iron production				Difference in water evaporated in coke oven	1,318	70	2,840
				(Moisture in coal: Old washery 15%, modern washery 10% "clean coal" plant 5%)			150
				Saving in coking time, say		10	20
				Increase in value of by-products @ -/1 per ton of coal		100	
				Increase in value of by-products @ -/3 per ton of coal			406
				Reduction in coke handling @ -/1	1,790	7	3,960
				Reduction in coke transport to blast furnace @ 3/4	1,310	220	433
				Reduction in limestone required @ 6/-	990	297	564
				Reduction in slag disposal @ 1/8	1,370	114	222
				No credit taken for:			
				Lower operating cost of cleaning process		—	—
				Faster driving of blast furnace		—	—
				Better quality of pig iron		£1,896	£4,498
The above credit balance is equivalent to a saving:							
Per ton of slack				s. d.			
Per ton of large coke				1/1			
Per ton of pig iron				2/3			
				2/5			
				2/1			
				5/2			
				5/1			

In the concluding paragraphs of the Cantor Lectures delivered before the Royal Society of Arts in 1925, I stated:

“In order to give the directing mind of the modern fuel technologist full scope, he must have supplied to him a coal containing a minimum of extraneous matter so that the working results are not left to the uncontrollable effects of these chance impurities, but are subject to tolerably exact prediction, possibly involving calculated and pre-determined additions of necessary correctives.

“Though it is never safe to prophesy, I make bold to suggest that within very few years the carbonizing industries, which are mainly concerned in the efficient recovery of the intrinsic value of coal, will feel constrained to insist for their raw material on coal containing only a fraction of the proportion of mineral matter which is customary today. I further believe that the provision of such a commodity will be technically possible and commercially profitable, and that it will be of economic advantage both to supplier and user.”

The work done since then has shown the way in which this object can be achieved and the general application of the principle of preparing coal free from detached mineral impurities is only a question of time.

# COAL CLEANING PROBLEMS OF TODAY

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## INTRODUCTION

Looking over the present problems of coal cleaning, one realizes at once that in dealing with this question many factors have to be observed and considered. These factors vary in importance and nature with particular cases. No systematic order can be given them; each problem must be solved as a separate case. Being a product of nature, coal is of the most varying composition, as also are the desired products derived therefrom. These products change in price and structure according to the demands of the market, which are different from place to place, and also according to the changing demands brought about by industrial and engineering development which creates new uses and new means of utilization of the products of coal. Examples of this are to be found in the use of coal dust as boiler fuel, and perhaps even motor fuel, and in the hydrogenation of coal. Finally, an important part is played by the freight rates to the different localities of consumption.

Plainly, therefore, it is impossible to offer in one short paper an exhaustive discussion of everything that is concerned with the problem of coal cleaning. Neither is it possible to discuss particular designs and constructions of coal cleaning apparatus; so I must presume that the principal methods of cleaning coal are known. Starting with present conditions, I shall try to point out the principal needs and tendencies of development, and shall outline the methods that may be used for solving the problem of coal cleaning with the greatest efficiency.

The significant feature of recent development is chiefly the aim to find the relations between the material properties of coal and the possibilities of cleaning it in a scientifically exact way, not only in regard to its macrostructure but in regard to its microstructure as well. I shall deal first with this question; next—and in connection with this—I shall examine the practical execution of the process of cleaning; and finally, I shall discuss several economic considerations.

## SOMETHING ABOUT THE THEORETICAL FOUNDATIONS OF COAL CLEANING

In regard to the material properties of coal, both its physical and chemical nature play a part in the process of cleaning. To simplify the discussion we shall classify coal in the following manner:

1. Anthracite and low-volatile coal, up to about 15 per cent volatile matter, which can be used for briquetting, as domestic, boiler, and producer fuel; in short, called "low-volatile-coal."

2. Bituminous coals which, mixed or unmixed, are used as fine coal (below 10 mm. size) for high and low-temperature carbonization, called "coking-coals."

3. Bituminous coals, which chiefly serve the gas industry or are used in flame-furnaces, etc., collectively called gas-coals.

4. Coals, which are suitable for producing oils and are called "oil-coals." They are not yet, but probably will be in the future, the subject of a special cleaning method.

A marketable by-product of all those coals is the coal-dust, which is used in an increasing extent as boiler fuel.

### PHYSICAL PROPERTIES

Discussing the physical properties of coal, we shall omit the specific gravity, since we shall deal with this point further on in connection with the impurities of coal. At present only the hardness and sizing of lump-coal shall be discussed. The sizing of lump-coal especially is an important factor in price-making and the marketing of the coal, as well as in deciding how the cleaning shall be carried out.

Lump-coal, as it is picked from the mine-run is on an average larger than 100 mm. in diameter. It is sold without further treatment, unless it is crushed for special purposes, as coking, etc. The pieces are separated by screens, which, for hygienic and economic reasons, are equipped with dust-collectors. They are cleaned by means of dry separation, belt-picking, etc.

Nothing in particular need be said about this cleaning method, which is adaptable for all coals of large enough size.

Having in mind European conditions, all coal smaller in size than about 100 mm. in diameter can be divided into two classes. First is the coarse coal from 100 mm. to about 10 mm. in diameter; second, is the fine coal from 10 mm. down.

The sizes below 0.3 mm. are called "dust" when in dry state; "sludge," when wet. The coarse coal from 100 to 10 mm. is, in all

cases, sold as "cube"—or "nut-coal" of different size and marking. It is cleaned either before or after screening.

The fine coal, however, is probably in most cases separated from the coarse material *before* washing.

Coking coal must always be smaller than 10 mm. in size and therefore requires no particular care, as regards breakage while being cleaned. Non-coking coal, however, is judged according to the size of lumps, and much breakage in this case will reduce considerably the price of the clean product. While coking-coal will stand any kind of handling, the friable non-coking coal must be mined and treated most carefully, in order to bring about the largest possible output of lump and nut-coal.

This however is not always so, and, looking at the steadily growing importance of coal-dust as fuel, it may well be said, that a large amount of dust, even in case of non-coking coal is no longer disadvantageous if preparation is not necessary or the fines are in a reasonably pure state.

It is most important for the efficiency of all cleaning methods to determine the ratio at which the different sizes will appear in the raw, middle, and final products. This is of special importance since the properties of the coal vary widely in different sizes. Screening, therefore, must be done according to certain standards and its fractions must be thoroughly investigated especially in case of fine coal. I shall deal with this point in detail in a later part of my paper.

#### CHEMICAL PROPERTIES VOLATILE-CONTENT

Amongst the chemical characteristics of the coal the volatile content chiefly determines the applicability of a coal to certain purposes. It is known, for instance, what the range of volatile matter must be for a coking coal, or which low volatile coal is especially suited for briquetting, etc. This volatile content, however, does not influence, nor is it influenced by, the process of cleaning. But research has proven that in regard to the suitability of coal for certain purposes its different constituents are of prevalent importance.

#### CONSTITUENTS OF THE PURE COAL

It has been known for considerable time, and shown by several investigators, as, for example, Mr. Lessing, that pure coal, free from slate, consists of vitrain, durain, and fusain. I shall omit the

clarain because of its subordinate importance and its close relation to vitrain.

All of these constituents change, in their reaction to technical treatment, according to their genetic circumstances and their state of coal-formation. Vitrain always outweighs quantitatively the other constituents. It occurs in anthracite as well as in highest volatile coals. In coking coal it is the true carrier of the coking property. The durain, or dull coal, is generally distinguished by its high content of volatile matter. Both constituents consist of high molecular weight carbon compounds.

Durain, it is claimed, is especially suited for making oil from coal, which, however, still remains to be further investigated. The third component, fusain, has to be considered a mineral charcoal with high content of amorphous carbon. It is very lean as regards volatile matter. While vitrain and durain, during carbonization, go through a plastic stage, the fusain remains fine-grained, with a highly detrimental effect on the coking power of coal. This influence, however, becomes evident only if the fusain is mixed with pure vitrain to the extent of about 20 per cent.<sup>1</sup>

It still remains to be investigated, whether or not such a high amount of pure fusain is already found in raw coal. Since it is most friable, it is easily possible, that it appears especially in fine coal sometimes increasing from 5 per cent in the raw coal to 25 per cent in the finished product. Therefore the separation of this fusain content mainly from fine coals is of great importance and we shall see, later, how this problem is being attacked in more or less promising manner.

In summary it may be said, that all coal-seams show differences in their content of these three ingredients and constant survey must be made, in order to determine the applicability of the coal for a given purpose.

It is commonly known, that by mixing high- and low-volatile coal or adding low-temperature coke good coke can be produced. But the scientific explanation or rule has to be the subject of more close investigation.

#### “COALPETROGRAPHY”

In order to work on the fundamentals of this question, it is necessary to obtain exact knowledge about the coal structure, and this is

<sup>1</sup> Glueckauf, Bd. 64 (1928), p. 81.

made possible by the "Coalpetrography." It has been especially developed in recent times to study the finer materials<sup>2</sup> from the cleaning process. They are imbedded in an easily hardening mass of special composition and subjected to a relief-grinding, so that the structural compilation, and kind and colors of the relief are easily distinguished. Thin sections are not very well suited for this study, neither is the usual observation through the binocular microscope. Vitrain shows in such a relief-grinding a smooth surface, uniform polish, and light-gray color. Durain has a nonhomogeneous compilation and partly granular or streaky structure, which are caused by clay-intercalations. Fusain is recognized by its lighter color and displays a vivid and well preserved fibrous texture. By further development of this method of investigation, it will also become possible to tell by observation through the microscope the quantitative ratio of the ingredients to the total substance.

The following determinations must therefore be made:

1. Determination of the maximum amount of lump-coal that can be obtained, when aiming at large size coal. At the same time investigations of the adaptability of the mine to production of lump and fine coal.
2. Tests on physical and chemical behavior of each singular coal-bed, in order to obtain the desired products in the most suitable manner.
3. Exhaustive study of the seams by means of the coalpetrography, so that the structure of the coal, especially below 1 mm. is known in all details.
4. Quantitative determination of the structure by immediate grinding analysis, complementary to the float- and sink-test and the usual microscopic observation.
5. Mixing programs should be worked out for the appropriate composition of coal for sale, coking, and for chemical purposes.

### DUST

Special mention remains to be made of the dust as present in the raw coal. All dry fine coal below 0.3 mm. in size is dust and can be used as fuel, if it is possible to produce it in suitable condition for this purpose. It also may be added to the fines of coking-coal, if it is sufficiently clean and has some coking properties. In this case it

<sup>2</sup> Stach, kohlenpetrographisches Practicum, 1928.

serves two purposes; first, it is disposed of without difficulty; second, it helps to reduce the water-content of the washed fine coal. This, however, will be discussed later. If the dust, untreated, is too dirty for either one of the above mentioned uses it must be washed, or mixed, as middle-product, with regular boiler-fuel and used for heating purposes in the mine. Dust always disturbs in the most serious manner the cleaning-process, be it wet or dry. Therefore it is a general practice of all cleaning methods to separate the dust first of all.

### WATER-CONTENT

The water-content of the raw coal is mostly of little practical importance. It varies from 2 to 7 per cent. Dry separation by means of air-separators, etc., is efficient enough for the dust removal, if the moisture does not exceed 4 to 5 per cent; moisture causes great difficulties and the dry separation becomes impossible, when the moisture-content is higher than 5 per cent.

The water-content, however, becomes an important factor, as regards the cleaned products when the coal is washed.

In the case of coking coal a certain amount of moisture from about 6, and a little more, per cent is considered desirable. Under certain conditions moisture up to 10 and even 12 per cent is permissible. But the situation is entirely different for non-coking coals. It is a general rule, that the less the moisture-content, the greater is the value of the coal. Four per cent is generally the maximum and usually there is no difficulty in obtaining this water-content in the coarser sizes.

The fines, however, take up the moisture very readily. Thus the finest sizes often increase the water-content of coking coal above the desired limit. Fines of non-coking coals can not be sold, unless they are dried in sludge-sumps.

Investigations on fines have brought about the following results:

It should be expected that the amount of water, taken up by small grains, increases proportionately to the increase of their surface; but in case of fines the surface gains more rapidly than the diameter. It is an established fact that half of the surface of fines from 0 to 10 mm. is made up by the dust below 0.3 mm. It has been shown, however, that there is a distinct change at the size of 1 mm. Grains of 0.5 to 1 mm. size take in proportion much more moisture than grains of 1 mm. size. Smaller grains down to 0.5 and 0.25 mm., however, do not show as disproportionate an increase.

After dewatering for 24 hours, the water-content of 1 to 2 mm. size is approximately 8 per cent. The sizes from 0.5 to 1 mm. contain no less than 35 per cent water, and the smallest sizes up to 50 per cent.<sup>3</sup> Dewatering is closely connected with the nature of the slate, that comes out with the raw coal. If there is much clay present, it has to be first removed, in order to dewater the cleaned coal without difficulties.

### SLATE

In general, it can be said that the quantity and kind of ingrown slate in a seam must be known. The quantity varies in the different screenings of the raw coal. It is determined by separating the coal in different sieve-fractions, which here again prove their importance, and by the ash analysis of those fractions. German bituminous, low-volatile coals often carry higher ash-contents in their coarser sizes. In case of high-volatile coals, however, it is the fine and finest material, especially the sludge, that is high in ash.

Experiments, which have been made in my laboratory and are to be published soon, have given very interesting information on this question. Different ash-curves were drawn, and showed in several cases the principal differences between coals from various places and also between brown-coal and bituminous coal. This work, however, has to be carried out still more systematically than before, in order to give reliable results.

### SPECIFIC GRAVITY AND WASHABILITY OF COAL

Corresponding to the slate-content of coal is the specific gravity of the different fractions. It varies for clean coal between 1.2 and 1.6, or 1.35 in average, according to the amount of slate that remains in the clean product. Refuse has a specific gravity of from 1.7 to 2.5, in case of sandstone; the range of pyrite is about 5.

Besides this, however, the constituents of the pure coal also carry some syngenetic ash. Vitrain is generally claimed to be the lowest in ash with a specific gravity of about 1.25; durain comes next with about 1.32, and lowest in rank is the fusain with about 1.5, because of the mineral constituents contained in the pores of the fossil plant-residues.<sup>4</sup> All these figures, however, are not conclusively determined and are still subject to discussion.

<sup>3</sup> Glueckauf, Bd. 63 (1927), p. 857.

<sup>4</sup> Glueckauf, Bd. 64 (1928), p. 630.

Since the separation of coal and slack by using their respective specific gravities in water is still the most reliable washing method, the ability of a coal to be cleaned is principally based on this process. Float- and sink-test or trial-jigging are the criterions. The resulting curve from those investigations is the well-known washability-curve. It records first the ash-content of each particular layer in the seam; a secondary curve reveals the average ash-content of the cleaned material, which has been stripped to a certain minimum ash-content of the lowest layer; a third curve gives a record of the average coal-content of the refuse at a certain point of the cleaning process. Many operating arrangements can be derived simply from this washability-curve.

### THE OPERATION OF THE CLEANING PROCESS

In discussing the operating part of the coal-cleaning the following points will be considered:

1. The cleaning of the coarse and fine coal.
2. The cleaning of the sludge.
3. The removal of fusain from coking coal.
4. The dewatering.
5. The removal of clay.
6. The drying.

Because of limited space, it is impossible to give detailed descriptions of certain constructions and designs in the field of coal cleaning. Therefore only the principal viewpoints will be mentioned and discussed.

### THE CLEANING OF COARSE AND FINE COAL.

For cleaning the coarse and fine coal there are quite a number of wet and dry processes in use. Washing is successfully done in jigs, rheo-washers, hydroseparators, by means of sand-flotation, etc. The dry methods are principally, the cleaning by means of centrifugal power, as in spiral-separators, the air-cleaning by so-called air-tables, the sand-air-process. The air-tables especially are coming more and more into close competition with the jigs. Spiral-separators are quite successful where simple cleaning conditions exist. The air-sand-process is still in state of development.

The wet process for cleaning coarse coal (above 10 mm.) and fine coal at least to 1 mm. can be carried out almost exactly corresponding to the optimum, which has been determined by the washability

curve. It can hardly be expected that any dry method will bring about better results in cleaning the above-mentioned sizes. However, in some cases, as for instance when the coal is not too intimately intergrown with rock, equal results may be obtained. But generally the dry process brings out a considerable amount of middle-products, which, in turn, would not be disadvantageous, if the mine itself uses large quantities of cheap unfinished products as boiler-fuel. The conclusions drawn herefrom are: to apply the dry method to easily separated fine coal; and to use the wet process for cleaning slate—intergrown coal. Some objection may be made, however, against the rather dull appearance of the wet-cleaned products. The dry process appears most promising when applied to the treatment of finer sizes than 1 mm. It would result in producing a dry coking coal, since the main cause of its moisture-content, the wet fines, is eliminated. All these considerations, however, hold good only for sizes larger than 0.3 mm. The dust can not be further separated in air because of unfavorable adhesiveness and suspension, and must therefore be separated in all cases prior to the cleaning. Even if the wet process is employed, the size below 1 mm. should be treated separately and not, as in the present practice, be left in the washed fines. It is advisable to separate, first, the sizes below 1 mm., by means of slit-screens, further to exhaust the dust below 0.3 mm., and then to clean the grains from 1 to 0.3 mm. separately.

In discussing the wet process it appears worth while to give some attention to the differences between the jigs and the rheo-washers. Rheo-washers are very efficient in case of slaty coals. For treatment of fines and sludge they are even claimed superior to jigs. The jigging process, however, is still the best suited for cleaning coarse coal.

As for investment and operating costs the following data are given:

Wet washing plants with jigs require about \$1,000 (Mk. 4.000), with rheo-washers about \$750 per ton-hour for capital cost.

In case of dry cleaning on tables the first investment, including lease for patents, usually corresponds to that of a modern washery. Through the elimination of careful sizing before washing, however, which is made possible in the newest types of washeries, some savings may be expected.

The investment costs for spiral-separators and their auxiliary equipment may be considerably less.

The over-head costs, for amortization and depreciation, will vary between 7, 5 and 4 cents supposing 15 per cent of capital and 2400 hours working time per annum. The power, (2 hp. per hour-ton), labor, and costs for upkeep will be about the same. The operating costs are lowest in case of spiral separators, being 2.5 cents and less. They vary widely for air-tables and are occasionally quoted at 7.5 cents, which will also hold true for jigging. Thus the total costs for cleaning will be from 6.15 cents to 15 cents and are influenced not only by the type of the washery employed but also by the character of the coal.

#### TREATMENT OF SLUDGE-COAL

The sludge from the wet process and dust, as far as it can not be used in such state, has to be further cleaned, which is done by flotation. The problem of flotation and machinery used in this process is sufficiently known; so I will concentrate attention only on the material treated. The sludge, finished by means of flotation, is of extremely high value, because of its low ash-content (from 2 to 3 per cent). The disturbing factor, however, in this case is the high water-content (from 25 to 30 per cent). It prohibits the use of this rich material in its original state, as well as of mixing it in unlimited quantities with fine coal. The dewatering, i.e., the drying process, which overcomes these difficulties, will be discussed later.

#### SEPARATION OF FUSAIN

This separation can be made by mechanical means. Extensive investigations on the removal of fusain, carried out in my laboratory, are based upon the proposal to use the morphological differences of the coal constituents where fusain is detrimental in a coking coal. Vitrain and fusain especially are different in their structure. The former is of cubic and irregular form, while the latter disintegrates into finely-shaped, acicular splints. It is therefore possible to separate fusain and vitrain by means of specially built screens. Fine slit-screens, which work either as spring or as shaking screens are best fitted for this purpose. They correspond well to the material to be separated because of their narrow longitudinal splits. Woven-sieves are a failure in this respect, since the rather oblong fusain-particles do not go readily through the square openings of the meshes.

The cleaning of fines below 1 mm. has been tried out in numerous tests with these special screens. The results in case of a raw sludge

that contained 40 per cent fusain and 30 per cent vitrain are remarkable. The results of the two cleaning methods, by flotation, woven-sieves, and split-screens are given below; in both cases the quantitative efficiency was 50 per cent.

CLEANING-METHOD	WOVEN-SIEVES	SLIT-SCREENS
Per cent fusain.....	55	75
Per cent vitrain.....	23	12

The experiments show that it is impossible to decrease the fusain-content sufficiently by means of woven-sieves, when coking-ability of the coal is desired. Screening through slit-screens, on the other hand, responds very well to the requirements made upon it.

The problem of separating vitrain and fusain has been attacked also by means of selective flotation, and we have had some recent results which show considerable promise for the future.

### DEWATERING

The dewatering of fine coal is still done in older-type washeries on slowly moving conveyers. A more modern installation are the dewatering-bins or pits. The washed coal including the total wash-water and sludge is sluiced into sumps. One part of the sludge remains in the coal, and the other part flows with the wash-water back into the "V-boxes" which are used for clarifying the dirty water. After the lapse of a certain time a balance between the sludge content and the wash-water is established.

Another practice that has been found very satisfactory is to de-water the washed material first by screening it through 0.5 mm. screens. All material, smaller in size than 0.5 mm., is thickened in "V-boxes" and is sifted through spring-screens with about 0.3 mm. openings. Thus the coal is dewatered to about 20 to 30 per cent water content and carried on belts to the pits. The separated water from the spring-screens is either wasted, as in the case of too high an ash-content, or floated, dried on filters, and the recovered coal then added to the dewatered coal. In all cases, however, where the material between 0.5 and 0.3 mm. can be used without further cleaning it is recommended to filter it in order to obtain a sufficient degree of dewatering. It then may be added to the clean fines or to the boiler fuel.

The dewatering, or rather the drying, of the sludge is most conveniently done in filters, which are widely used for this purpose. Drum-type filters usually designed as multiple compartment filters have, however, one serious disadvantage. The fact that they are fed from the outside causes many difficulties in keeping the filtercloth clean; the fine material has usually settled near the surface of the cloth and cannot be removed by the pressure that is usually applied for cleaning the pores. It has been tried, therefore, to introduce the slush inside the drum and to have the coarser material, which sinks to the bottom more readily than the finer particles, settle first on the cloth. The danger of plugging the pores in the filtercloth has been greatly reduced by this procedure.<sup>5</sup>

Other installations for dewatering are several types of centrifugal-dryers, which have found reception in America (U. S. A.), England, France, Belgium and Germany. The capacity of these centrifuges is claimed to be as high as 50 tons per hour.<sup>6</sup> The reduction in the water content is from 7 to 8 per cent water in the finished product, against 15 to 25 per cent in the untreated material. An interesting fact brought about by the dewatering in centrifuges is a reduction in ash also, which has been noticed in several cases. An explanation for this is, perhaps, the removal of some of the clay content which is carried away with the water.

#### REMOVAL OF CLAY

The removal of the clay from the sludge, as practiced at present, is based on the principle of converting the easily swelling clay particles into a colloidal solution in which they are carried away with the water. This solution of the clay is brought about by simply stirring water or by means of suitable electrolytes, as soda-water glass or Xnetogenate.<sup>7</sup> The coal particles which are surrounded by the clay and so somehow agglutinated, are liberated by this process and can easily be separated so as not to accompany the clay into the refuse. The coarse material settles down, while the clay-solution, with the finest coal-particles that have not gone to the bottom is pumped away. In order to accelerate the suspension of the clay in

<sup>5</sup> V. D. I.: Bd. 72 (1928), p. 1089.

<sup>6</sup> Iron and Coal Trades Review, vol. 111 (1925), p. 359. Glueckauf, Bd. 64 (1928), p. 1127/30.

<sup>7</sup> Zeitschrift des oberschlesischen Berg- und Hüttenmannischen Vereins, 1928, 7 Heft.

the water, air is blown through the whole mass. It may be mentioned that the above described slit-screens prove of very great convenience in this process also. Two distinct improvements are brought forward by this treatment; First: the refuse is higher in ash; second, the middle products are cleaner.

In addition to this, the time required to dewater the coking coals in the draining-bins is considerably shortened, since the absence of the water-binding clay-content helps greatly the removal of the water. Thus the draining-bins can be lighter and cheaper in construction, than would be necessary if the clay were not removed previously to the bin-storage.

An increase of the by-products is also a result of decreasing the water content by this treatment.

### THE DRYING PROCESS

Artificial drying of the cleaned fines is employed in all cases where coal for briquetting purposes is produced. Coking-coals, however, are treated to a surprisingly small extent in this direction. The upper limit of the moisture content in this case is 12 per cent; which means that, when slush is added it must be dry enough not to increase the moisture of the mixed product above the said limit. But even this amount is still higher than the desirable content of from 6 to 8 per cent water. The addition of this 4 to 6 per cent water in the coal going into the coke-ovens is hardly anything more than unnecessary ballast, which has to be evaporated, thus requiring additional heat for the carbonization, extending the coking-time, and decreasing the output of the ovens. The following table gives an impression of how the variation of the water content affects the coking-time and the output of by-product ovens.

Water-content.....	12.38 per cent	6 per cent
Coking-time.....	12 hr.	10 hr.
Output*.....	21.4 t/24 hr.	25.7 t/24 hr.

\* Ton = 1.000 kgm.

The table shows how, without increasing the number of ovens, but simply by reduction of the water content of the coal, the coke-production in this particular case can be increased 20.5 per cent with an increase of the gas output of 12.6 per cent.<sup>8</sup>

<sup>8</sup> Glueckauf, Bd. 63 (1927), p. 860.

## COMMERCIAL CONCLUSIONS

The rather limited space of this paper does not allow a detailed discussion of the commercial value of all operations connected with the problem of coal cleaning. Certain crystallized points, however, may be presented in this connection.

First of all, effort should be made to bring about the differentiation of the cleaned-products according to their value for individual purposes. The coke-producer for instance pays the same price for coal with 12 per cent water as that with 6 per cent. If he could be induced to evaluate the coal higher, the nearer it comes to the moisture content of 6 per cent, which is mostly desired for this use, the mine operator could easily pay additional attention and expense to the drying of his finished products. The same applies to non-coking coals, which in their market specifications are also given allowance for unnecessary water-content, involving freight expenses for water which could be spent on coal.

As for the ash content, the allowances usually given are 7 to 12 per cent for the non-coking coals, 7 to 8 per cent for coking coals, which results in 10 to 12 per cent ash in the coke produced. All these limits are, of course, made the basis for the extent of cleaning the coal. The situation, however, becomes different, as soon as the coke-producer and the coke-consumer are identical, as for instance in Germany, where the mines are combined with coke and steel plants. This brings about logically the aim to start at the very beginning with as pure materials as possible.

In short, it is desirable to differentiate more than before between various grades of quality. Thus the producer of coal will be enabled to operate the cleaning process under highly economical conditions.

Raw coal at present costs about \$3.60 (Mk. 15. -) in Germany. The price for the finished product ranges from \$7.60 (Mk. 32. -) for "Nut I," to \$2.62 (Mk. 11. -) for non-coking fines. Sludge is valued at about \$1.00 (Mk 4. -). This gives, varying with the conditions at each individual mine, an average price for all products of from \$3.80 (16 Mk.) to \$4.30 (Mk. 18. -). Considering the fact that about 10 per cent of the gross output is lost in the form of slate, the actual increase in the value of the cleaning-products is very little.

The importance or rather necessity of cleaning the coal, however, becomes evident, when taking into account the fact that raw coal cannot be sold in this state without seriously lowering its price.

Thus deducing that the cleaner products represent disproportion-

ately higher values than the original material, it again should be the practice to classify different grade products as distinctly as possible.

The development will probably be led automatically in this direction, as soon as coal becomes the principle raw material of the chemical industry. The production of highly qualified gases and nitrogen preparations, and the hydrogenation of coal have already proven their possible influence in this respect. Intentional and controlled dissection of the coal constituents is the outlook which offers itself for the further applicability of coal in this field.

The consumption of coal at the mine itself involves entirely different problems from those of the outside consumer.

"For sale" are all highly qualified products; "on stock," or for disposal in the mine are the materials which can only be cleaned under efforts that reach beyond their increase in value. On the other hand, it should not happen that one mine, for the sake of utilizing all "waste fuel," generates energy for which there is no demand; and another mine, because of dearth in middle-products, burns highly valuable finished material.

In order to obtain and keep efficiency in the operation of large mining areas a central power station must exist, where all excess energy is sent and from where all needed energy is taken. The coking industry in Germany has created the idea of centralized long distance transmission of gas, thus marketing highly qualified products that had to be considered as waste-products before. "Refuse" and "middle-products," as recovered in coal washeries, would highly justify all serious considerations of further treatment, as soon as the collieries would use and clean these materials collectively from several mines.

On the other hand, the utilization of the middle-products does not depend solely on the extent to which they are "clean," but may be rendered efficient by means of their use also. Several grate-constructions, for instance, are in existence that are especially fit for burning strongly intergrown material. The always troublesome dust may also be utilized by stokers that are designed for additional dust-firing.

In summary, it can be said, therefore, that many improvements, not only in the washing process itself, but also from the economical viewpoint, are still possible.

# GAS PURIFICATION IN RELATION TO COAL SULPHUR

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The purification of gas means properly the removal of all impurities that may interfere with its distribution or utilization; but it is significant of the injurious effects of sulphur compounds that in the gas industry the term "purification" is always understood to mean removal of sulphur. In fact, the actual use of the term is nearly always limited to the removal of hydrogen sulphide, in which form most of the sulphur occurs.

During the past ten years, our organization has been very actively engaged in research on gas purification, and this work has resulted in the introduction of radically new processes which are in large-scale operation in many plants in America, Europe and Japan.

The question has been asked whether these new developments might make possible the utilization of coals of higher sulphur content without the necessity of washing them. This paper will present the results of a study of this question.

## GASES DERIVED FROM COAL

The following gases of present industrial importance are manufactured from coal:

1. Coal gas made in by-product coke ovens or gas retorts.
2. Water gas principally made from the coke obtained as a by-product of coal gas manufacture, but also produced from anthracite and, in recent years, from certain grades of bituminous coals direct.
3. Producer gas made from coal or coke.

In the processes of manufacturing any of these gases, part of the sulphur in the coal goes into the gas and must be removed if the gas is to be used for domestic purposes or for certain industrial purposes. Hydrogen sulphide is always the predominant sulphur compound and state regulations require a very high efficiency of extraction. The actual proportion of hydrogen sulphide in purified city gas is less than  $\frac{1}{16}$  grain per 100 cubic feet. The sulphur compounds, other than hydrogen sulphide, are of organic nature and with the exception of carbon disulphide are present in very small amounts. Where low sulphur coals are used the removal of carbon disulphide is not under-

taken. Regulations usually specify less than 30 grains per 100 cubic feet of organic sulphur.

#### REMOVAL OF SULPHUR FROM GAS

Until very recently, the processes of sulphur removal have been applied exclusively to coal gas and water gas produced primarily for domestic utilization. Industrial consumers of such gas have obtained the incidental advantages of purification, but the removal of sulphur from industrial gas *per se* has been slow of introduction. This tardiness has been due mainly to the cumbersome and expensive apparatus and process which had become standardized and considered necessary by the gas industry until a few years ago.

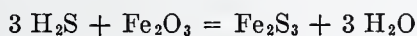
This universally adopted process was the so-called dry purification which consists in passing the gas through large boxes made of cast iron, steel or even wood and filled with hydrated iron oxide mixed with some bulky material such as wood shavings, ground corncobs, etc. During the past ten years, The Koppers Company has introduced various processes of liquid purification characterized by the use of certain aqueous solutions for washing the gas to remove the hydrogen sulphide. There are now over 60 liquid purification plants in operation with a total capacity of over 500,000,000 cubic feet of gas per day. The adoption of liquid purification has not only had certain direct advantages, but has stimulated the cheapening of dry purification, so that the expense of sulphur removal is now a very small fraction of the cost of gas manufacture and gas purification has been rendered feasible and attractive for many industries which were formerly forced to use unpurified gas. However, it must be remembered that most industrial and domestic gas is being produced from coals of relatively low sulphur content. In America, enormous quantities of coal with less than 1 per cent of sulphur are available at low price and as a rule there must be very special local conditions to favor the use of coal containing more than 1.50 per cent of sulphur. Furthermore, in any consideration of the possibilities of utilizing higher sulphur coals for gas manufacture, an important fact must be emphasized, viz., *neither the dry process nor the liquid processes of gas purification remove any appreciable amounts of organic sulphur compounds*. The significance of this will be discussed later. When the amount of organic sulphur exceeds a certain limit, it must be removed by a separate process.

For the purposes of this paper, a brief description of the sulphur removal processes will now be given and will include the following:

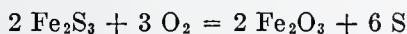
1. Dry purification.
2. Liquid purification: (a) The Seaboard or non-recovery process; (b) sulphur recovery processes.
3. Removal of organic sulphur: (a) Catalytic process; (b) oil scrubbing.

#### DRY PURIFICATION<sup>1</sup>

The apparatus employed in dry purification consists in a series of three or four boxes filled with hydrated iron oxide, mixed with wood chips or shavings, ground corncobs or other bulky material. The hydrogen sulphide reacts with the iron oxide forming ferric sulphide as follows:



The iron oxide can be regenerated by exposing the ferric sulphide to air when the following reaction takes place:



The sulphiding and regeneration can be conducted repeatedly until the amount of free sulphur has been built up to 40 to 50 per cent of the spent oxide. The material must then be discarded. Different schemes of "rotating" the boxes are employed; i.e., changing their order from time to time with respect to the flow of gas so as to obtain the best efficiency of utilization of the oxide.

Regeneration may be accomplished as follows:

1. Intermittent revivification. The material is removed from the boxes and spread out on the ground and turned over mechanically from time to time until it is thoroughly exposed to the action of the air.

2. Continuous revivification. A small amount of air is admitted to the gas so that the two reactions of sulphiding and regeneration take place practically simultaneously. Very often this method is combined with No. 1. This introduction of air certainly saves labor, increases the capacity of the purifying boxes and reduces the expense of purification, but has the disadvantage that the excess oxygen favors corrosion in the distribution system and appliances and in some cases may cause trouble by reacting with certain organic compounds to form gummy or resinous deposits.

<sup>1</sup> For further information on dry purification, refer to:

(1) Alwyne Meade, *Modern Gasworks Practice*, 2d ed., Chapter 18.

(2) American Gas Association, *Report of Chemical Committee, 1926*, Chapter 11 by F. W. Sperr, Jr.

3. Revivification *in situ*. In this method, the box containing the oxide to be regenerated is disconnected from the series and air is carefully introduced until the material is thoroughly reoxidized. This practice involves a considerable element of danger and is not often resorted to. A considerable amount of heat is generated by the oxidizing reaction so that unless great care is taken, the oxide may catch fire and a serious explosion may result.

A large amount of ground space is required for the oxide boxes and for the storage and revivifying space in dry purification. The area required for a plant handling 20,000,000 cubic feet of coal gas per 24 hours is about 90,000 square feet.

The characteristic dry purification apparatus of a number of years ago was very cumbersome and costly. The apparatus was usually housed in expensive buildings. The boxes were rectangular and quite shallow. Cast iron was frequently employed. Modern practice has introduced a much cheaper type of construction. The present boxes are of steel, often cylindrical and characterized by much greater depth. Each box usually contains two 5-foot layers of purifying material, instead of a single layer. The boxes are built out of doors with a very simple lagging as protection against changes of atmospheric temperature. Mechanical devices are used for loading and unloading the boxes. In the more recent plants, the steel sheets are welded instead of riveted.

#### LIQUID PURIFICATION WITHOUT SULPHUR RECOVERY

The first liquid process of gas purification was introduced by The Koppers Company in 1920 and is known as the "Seaboard Process" because it was developed at the plant of the Seaboard By-Product Coke Company, Jersey City, N. J. The original Seaboard plant has been in operation for eight years and a large number of other plants of this type have also been installed during this period.<sup>2</sup> The apparatus consists of a tower having two main sections designated as the absorber and the actifier, together with air blowers, circulating pumps, and other minor auxiliary apparatus. The absorber and actifier are filled with suitable packing, e.g., coke, spiral tile, or

<sup>2</sup> For further information on the Seaboard Process, see

(1) F. W. Sperr, Jr., Seaboard Liquid Process of Gas Purification, American Gas Association—Technical Section Sessions (1921), p. 282.

(2) F. W. Sperr, Jr., Progress in Liquid Purification—American Gas Association Proceedings, 1923, p. 1200.

(3) Fred W. Seymour, Liquid Purification at Battle Creek, Gas Age-Record, 1922, p. 765.

wooden hurdles. The absorbing medium consists of a dilute solution of sodium carbonate (commercial soda ash), the ordinary strength of which is equivalent to from 1 to 3 per cent  $\text{Na}_2\text{CO}_3$ . This solution is pumped from a sump over the absorber from which it flows by gravity into the actifier and thence back to the sump. The gas passes through the absorber in intimate contact with the solution which removes from 85 to 95 per cent of the hydrogen sulphide, depending upon the design of the plant with relation to the amount of gas and the sulphur content treated. Some of the carbon dioxide and most of the hydrocyanic acid in the gas are also removed. Practically complete extraction of the hydrogen sulphide may be accomplished by two absorbers operated in series, but a single absorber is sufficient for most industrial purposes and in city gas plants the small amount of hydrogen sulphide remaining is removed in small boxes filled with iron oxide purifying material.

The solution containing the absorbed impurities flows down through the actifier through which air is blown by a fan. The volume of air required is from two to three times the volume of gas purified. The air removes the hydrogen sulphide and regenerates the solution so that it can be used over and over again. Some soda is used up in the formation of sodium thiosulphate and sodium thiocyanate and in mechanical losses, but the amount so consumed is very small. The usual consumption of sodium carbonate in the purification of coal gas is about 1 pound for every 8 pounds of hydrogen sulphide removed, some plants, however, showing much lower soda consumption figures than this.

The hydrogen sulphide in the actifier air is greatly diluted and in certain districts this may simply be discharged into the atmosphere through a tall stack. In other locations where the hydrogen sulphide would be objectionable, the actifier air is consumed in boiler plants, gas producers, water gas apparatus, etc., and may be used as the combustion air in by-product coke ovens or gas retort settings.

### SULPHUR RECOVERY PROCESSES<sup>3</sup>

There are several processes in which the sulphur present in the gas

<sup>3</sup> For further information on the Sulphur Recovery Processes, see

(1) F. W. Sperr, Jr., *New Methods of Gas Purification*, Gas Age-Record, July, 1926, p. 73.

(2) American Gas Association, *Report of Chemical Committee*, 1926, Chapter 11, by F. W. Sperr, Jr.

as hydrogen sulphide is recovered as elemental sulphur. In all of these a solution of sodium carbonate is used to scrub the gas as in the case of the Seaboard Process, but the different processes are distinguished by the material which is added to this solution to effect the conversion of the hydrogen sulphide to elemental sulphur. We have the following principal processes:

1. *The Iron Process*—characterized by the employment of an iron compound usually in suspension in the alkaline solution. The principle of this process was developed by M. D. Mann, Jr., and R. B. Lebo, of the Standard Oil Development Company.

2. *The Nickel Process*—using a nickel compound as a catalyst suspended in the alkaline solution. This was developed by the Pacific Gas and Electric Company, under the direction of W. S. Yard, Vice President.

3. *The Thylox Process*—employing a new material known as “Thylox” in combination with sodium carbonate so as to form a substantially neutral solution without any suspended material. This has recently been developed by The Koppers Company which also owns the patent rights to the Iron and Nickel Processes.

The apparatus employed in the Sulphur Recovery Processes consists in an absorber differing little from the absorber employed in the Seaboard Process, and a thionizer in which the solution is aerated. The proportion of air used is much smaller than in the Seaboard Process, and the air is introduced in a state of fine subdivision so as to perform the oxidizing reactions and at the same time effect a separation of the sulphur by “flotation.” This phenomenon of flotation is familiar to all metallurgical engineers. It is accomplished by the adhesion of minute air bubbles to the sulphur particles so that these are lifted to the surface of the liquid of the solution in the form of a characteristic foam, from which the sulphur is readily separated by filtration. There are two main types of thionizers. In one, compressed air is injected into the solution and is distributed by a porous material, such as canvas. In the second, the air is beaten into the solution by a mechanical rotor.

The application of the different Sulphur Recovery Processes depends upon local conditions. The Nickel Process is restricted to gases low in hydrocyanic acid, such as water gas, because the hydrocyanic acid reacts with the nickel and soda, forming an inert compound. The Iron Process and Thylox Process are generally applicable to all gases. The purification efficiency of the Sulphur Recovery

Processes is very high, a removal of 97 per cent of the hydrogen sulphide together with complete removal of the hydrocyanic acid being readily obtainable in a single absorber.

### COMPARISON OF DRY AND LIQUID PURIFICATION

The choice of dry purification or of one of the several liquid purification processes depends so much on local conditions, such as the location of the purification apparatus with reference to the main plant, cost of power consumed and labor, pressure of gas to be purified, sulphur content of gas, etc., that a complete discussion would require much more space than can be given here. The following general observations may be made:

1. The simplest and most economical process is the Seaboard or Non-recovery Process. This is particularly true in the case of industrial gases where complete removal of hydrogen sulphide is not required; but even where complete removal is essential, the costs of installation and operation of this process are much less than of any other.

2. Where the actifier air from the Seaboard Process cannot be discharged into the atmosphere and where no means are available for consuming this air, dry purification or one of the Sulphur Recovery Liquid Purification Processes must be adopted.

3. Liquid purification processes offer the following advantages:

- a. Much smaller ground area required.
- b. Practically complete removal of hydrocyanic acid which is not accomplished in dry purification.
- c. Improved labor conditions.
- d. Liquid purification can be applied to gas under any pressure, while dry boxes are objectionable for gas of over 5 pounds and should preferably be employed at much less pressure.
- e. There is much less resistance to the flow of gas in liquid purification apparatus than in oxide boxes and the expense for pumping is thus substantially less in the former case.
- f. The admission of air to the gas necessary for the economical operation of dry purification systems is objectionable on account of favoring corrosion in the distribution system and appliances.
- g. There is some risk of explosion in the operation of oxide boxes through excessive heating in the presence of explosive mixtures of gas and air. This sort of risk is reduced to a minimum in liquid purification systems.

Where the gas is to be purified at low pressures and where ground area is cheap, the costs of dry purification and of the Sulphur Recovery Processes may be regarded as approximately the same. The choice will, therefore, depend upon the local importance of the foregoing considerations.

#### REMOVAL OF ORGANIC SULPHUR

For practical purposes, the organic sulphur present in the various commercial gases produced from coal may be considered as carbon disulphide. According to K. L. Dawson,<sup>4</sup> five-sixths of the total organic sulphur exists as carbon disulphide and most of the remainder is thiophene ( $C_4H_4S$ ).

Legal restrictions in England were formerly as severe with respect to carbon disulphide as for hydrogen sulphide. The removal of the carbon disulphide was accomplished by means of lime boxes. This was an expensive process, as any carbon dioxide in the gas combined with and neutralized the lime so that large quantities of this material were required. The regulations applying to organic sulphur were abolished in England in 1905, and on account of the high sulphur coals used in that country the city gas, as distributed, usually contains from 35 to 50 grains of organic sulphur per 100 cubic feet. In America, the statutory limit is usually 30 grains per 100 cubic feet and most city gas contains much less than this amount.<sup>5</sup> K. L. Dawson states that the experience of the City of Halifax indicates that odor complaints traceable to the quality of the gas practically disappear when the sulphur is kept below 35 grains per 100 cubic feet, and this is the legal limit for Nova Scotia.

There are several processes for the removal of carbon disulphide based on the treatment of the gas with some catalytic material which effects the conversion of the carbon disulphide to hydrogen sulphide which is then removed by the usual methods. Of these catalytic processes, one of the best known is the Carpenter-Evans Process which consists in heating the gas to about  $420^{\circ}C$ ., then passing it over fireclay balls impregnated with a nickel compound. This process has been used on a large scale by the South Metropolitan Gas Company of London.

<sup>4</sup> Journal of the Engineering Institute of Canada, April, 1928, p. 266.

<sup>5</sup> Several cities have municipal regulations limiting the organic sulphur to 20 or 25 grains per 100 cubic feet. The limit prescribed by Omaha is 15 grains (Amer. Gas Assoc. Monthly, April, 1923, p. 251).

In America, there are two gas companies which are regularly removing carbon disulphide. These are the Portland Gas and Coke Company, of Portland, Oregon,<sup>6</sup> and the Nova Scotia Tramways and Power Company, Ltd., of Halifax, N. S. Both of these companies remove the organic sulphur by scrubbing the gas with a petroleum oil and it would appear that a process of this type is the most economical and satisfactory for the purpose—at least under American conditions. A description of the oil scrubbing process with very complete information as to technical details and cost figures has recently been published by Mr. K. L. Dawson.<sup>7</sup>

The efficiency of the oil scrubbing process in the Halifax plant is low, but sufficient to bring the organic sulphur below the legal limit. Mr. E. L. Hall, of the Portland Gas Company, states that the removal of 75 per cent of the organic sulphur is entirely feasible. He points out that the oil scrubbing process has the incidental advantages of removing naphthalene; of eliminating gum-forming hydrocarbons and of recovering benzol, the sale of which partially offsets the cost of operation.

#### COST OF SULPHUR REMOVAL

Any answer to the main question of this paper, viz., the relation of gas purification to the problem of coal washing requires knowledge of the effect of variations in percentage of coal sulphur on the cost of gas purification. This in turn necessitates practical information as to the relation between the percentage of coal sulphur and the amount of hydrogen sulphide and organic sulphur in the different gases, together with data concerning the relation between the amount of sulphur in the gas and the cost of purification. A study of this sort is one of extraordinary complexity. There are so many variable factors affecting the relations between the sulphur in the coal and the sulphur in the gas and between the sulphur in the gas and the cost purification that the proposition of condensing these possibilities into a few general conclusions that would serve the practical purpose of this paper appears almost hopeless. The following statements are made on the basis of rough approximations to what might be considered as typical conditions and it is well realized that they may be open to a great deal of criticism if applied to a variety of specific cases.

<sup>6</sup> American Gas Association Proceedings, 1923, p. 1197.

<sup>7</sup> Notes on Removal of Carbon-Sulphur Compounds from Coal Gas by Oil Washing, K. L. Dawson, Jour. Eng. Inst. of Canada, April, 1928, p. 266.

The cost of sulphur removal depends upon a large number of conditions which vary greatly in different plants. The size of the plant, the prices of power, steam, labor, purifying material, etc., must all be taken into consideration together with gas pressure conditions, value of ground area, amount of hydrogen sulphide, organic sulphur and hydrocyanic acid in the gas, credit for sulphur and other by-products, etc. The important consideration is not the absolute cost of purification, but the question, How does this cost vary with different amounts of sulphur in the gas? Our data in this respect are very incomplete and approximate not only because of variation in local conditions, but because of the fact that American gas companies generally deal with gas of relatively low sulphur content, while experience with the purification of high sulphur gases is principally obtained in European plants operating under quite different conditions.

The cost of purification by the dry process and by the Sulphur Recovery Processes may be taken as approximately the same and is practically directly proportional to the amount of hydrogen sulphide in the gas. When the gas contains more than 1000 grains of  $\text{H}_2\text{S}$  per 100 cubic feet, the cost of dry purification probably exceeds a direct proportion.<sup>8</sup> It may be assumed for the purposes of this paper that the sum of the fixed and operating costs for removing hydrogen sulphide by these processes will increase at the rate of 0.35 cent per 1000 cubic feet for each increase of 100 grains  $\text{H}_2\text{S}$  per 100 cubic feet.

There is practically no limit to the amount of hydrogen sulphide which can be successfully removed by the Seaboard Process. One plant is employing this process for the treatment of natural gas containing 7000 grains of hydrogen sulphide per 100 cubic feet. The cost of purification by the Seaboard Process increases somewhat less rapidly than a direct proportion to the amount of hydrogen sulphide; but for our purposes, it may be assumed that the rate of increase is about 0.1 cent per 1000 cubic feet for each increase of 100 grains  $\text{H}_2\text{S}$  per 100 cubic feet.

The removal of the organic sulphur is a costly operation in spite of the small quantities usually present. K. L. Dawson states that the net operating cost for treating 96,000,000 cubic feet of gas per year at Halifax was 1.66 cents per 1000 cubic feet. This does not

<sup>8</sup> The Sulphur Recovery Processes have not yet been applied to gas containing more than 600 grains  $\text{H}_2\text{S}$  per 100 cubic feet.

include fixed charges and is based on a credit for benzol recovered although no allowance is made for the heating value of the benzol removed from the gas. As previously stated, the efficiency of removal of the organic sulphur in this plant was comparatively low.

The cost of removing organic sulphur by the Carpenter-Evans Process on a 15,000,000-cubic foot plant is given by Meade<sup>9</sup> as 0.7715d or 1.54 cents per 1000 cubic feet. This is probably a pre-war figure and would be higher in America today.

We have no data on which to base an estimate of the cost of removing different amounts of organic sulphur. It is very probable that where the removal of organic sulphur is necessary the total expense required is at least equal to the cost of removing the hydrogen sulphide produced in the same gas from the same coal.

### COAL GAS

*Sulphur in Coal Gas.* The distribution of sulphur in coal gas manufacture depends on several factors of which the more important are the type of carbonization apparatus, the temperature and time of carbonization, the character of the constituents forming the ash, and the character of the coal itself. Data from recent operating records of three by-product coke plants averaged for a period of one month each are shown in Table I. In these plants, a low-sulphur coal mixture was used containing approximately 30 per cent low-volatile coal (Pocahontas) and 70 per cent high-volatile Eastern coals. The figures indicate that from 25.7 to 29.2 per cent of the sulphur in the coal appears as hydrogen sulphide in the gas entering the purification apparatus. Similar studies published by F. M. Reiter<sup>10</sup> and A. Weindel<sup>11</sup> show 28.7 and 30.6 per cent respectively. The laboratory investigations of S. Quarfort<sup>12</sup> gave results of the same general order.

It may, therefore, be assumed that under average conditions about 28 per cent of the sulphur in the coal is found as  $H_2S$ , which must be removed by the purification apparatus.

<sup>9</sup> Modern Gas Works Practice, 1921, page 614.

<sup>10</sup> Study of Elements in Coal Carbonization, F. M. Reiter, Blast Fce. and Steel Plant, vol. 16, 1928, p. 635.

<sup>11</sup> Sulphur Balance in Coke Oven Operation, A. Weindel, Gas Age-Record, vol. 59, 1927, p. 775.

<sup>12</sup> The Relation between the Analyses of Coal and the Substances formed in Gas Production, S. Quarfort, Chem. Abst., vol. 20, 1926, p. 3072.

K. L. Dawson states that under average conditions at the Halifax Gas Works there is a definite relation between the sulphur in the coal and the organic sulphur in the gas. According to his figures, the number of grains of organic sulphur in gas produced from continuous vertical retorts may be found by multiplying the percentage of sulphur in the coal by 15. In other words, with coal containing 2 per cent of sulphur, the gas from such retorts would contain 30 grains of organic sulphur per 100 cubic feet. The rate of increase of organic sulphur in the case of horizontal retorts and inclined slot retorts is greater. In these cases, with coal containing more than 1

TABLE I  
SULPHUR DISTRIBUTION IN BY-PRODUCT COKING

	PER CENT SULPHUR IN COAL	PER CENT SULPHUR IN COKE	H <sub>2</sub> S IN GAS*	PER CENT TOTAL SULPHUR ELIMI- NATED	PER CENT TOTAL SULPHUR RE- TAINED IN COKE	PER CENT TOTAL SULPHUR AS H <sub>2</sub> S IN GAS*	PER CENT SULPHUR UNAC- COUNTED FOR
			<i>grains per 100 cubic feet</i>				
Chicago By-Product Coke Company.....	0.67	0.57	224	35.2	64.8	25.7	9.5
Minnesota By-Product Coke Company.....	0.65	0.57	230	34.4	65.6	27.2	7.2
Seaboard By-Product Coke Company.....	0.66	0.57	260	36.3	63.7	29.2	7.1

\* Gas samples taken just after the "final coolers" and before the purification apparatus.

The organic sulphur in the gas in these plants is not regularly tested, but is usually less than 15 grains per 100 cubic feet.

per cent of sulphur, the amount of organic sulphur in the gas is nearly a straight line function of the sulphur in the coal. For inclined retorts, the relation is approximately  $S = 40C - 18$ ,<sup>13</sup> where  $S$  represents the number of grains of organic sulphur per 100 cubic feet of gas and  $C$  represents the percentage of sulphur in the coal. For horizontal retorts, the relation is approximately  $S = 33C - 18$ .<sup>13</sup> In the figures shown in Table II,<sup>14</sup> there is no such well defined

<sup>13</sup> These formulae are, of course, to be applied only to coal containing more than 1 per cent of sulphur.

<sup>14</sup> Table II is a copy of figures published by O. P. Brysch and J. F. Byrne, Proceedings of the American Gas Association, 1927, p. 1463.

relation, but this is not conclusive on account of the short periods during which the tests were made. It is to be regretted that more information is not available to show the amount of organic sulphur produced in the coking of high sulphur coals, but it is probably conservative to assume that the rate of increase will be at least equivalent to 15 grains of organic sulphur for each per cent of sulphur in the coal and that the actual amount in certain cases may be much greater than this.

*Sulphur in Coke.* The effect of sulphur and associated impurities on coke quality is generally a more important consideration than their effect on the costs of gas purification. Higher sulphur usually means

TABLE II

DISTRIBUTION OF SULPHUR IN THE COAL TO ORGANIC SULPHUR IN GAS AND SULPHUR IN RESULTING COKE

TEST NUMBER	PER CENT SULPHUR IN COAL	ORGANIC SULPHUR IN GAS		SULPHUR IN COKE	
		Grains sulphur per 100 cubic feet	Calculated as per cent of total sulphur in coal charged	Sulphur in total coke by analysis	Calculated as per cent of total sulphur in coal charged
A.....	4.56	103	1.8	3.91	60.0
B.....	3.59	67	1.4	3.04	60.4
C.....	3.65	51	1.0	2.76	54.9
D.....	1.80	28	1.0	1.16	50.1
E.....	1.74	30	1.2	1.27	51.5
F.....	0.79	16	1.4	0.65	59.4
G.....	0.93	19	1.4	0.77	59.3

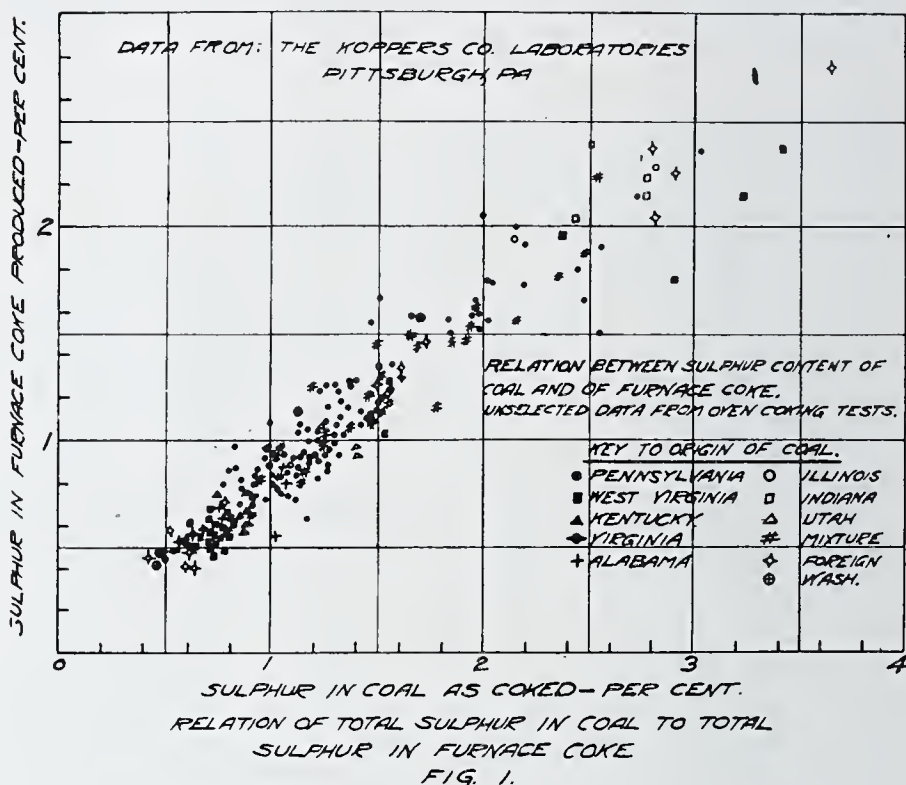
higher ash. Higher sulphur nearly always means a lower fusing point of ash. Higher sulphur, higher ash, and lower fusing point of ash make an inferior coke whether for domestic, water gas, or metallurgical purposes.

The relation between the sulphur content and value of blast furnace coke has been studied by T. L. Joseph,<sup>15</sup> of the United States Bureau of Mines. With coke at \$6.00 per ton, an increase of 0.5 per cent of sulphur in the coke involves an increase of \$1.30 in the cost of making a ton of pig iron. With coke at \$8.00 per ton, the increased cost of making pig iron is about \$1.65 per ton of metal. For practical pur-

<sup>15</sup> Effect of Sulphur on Blast Furnace Process, Min. and Met., September, 1924.

poses, it may be assumed that one ton of coke is required per ton of pig iron so that the effect of the sulphur on the value of the coke is quantitatively the same as the consequent increase in the cost of making pig iron.

The effect of sulphur on the values of water gas coke and domestic coke has not been and probably cannot be so precisely worked out. In the case of domestic coke, competitive conditions are paramount. This is also true where water gas coke is sold in competition, and in



either of such cases, that coal or mixture of coals must be selected which will best meet competition. On the other hand, where all the coke produced is used by the gas company for water gas manufacture the primary considerations are the increased cost of purifying the water gas and the probable higher ash and lower fusing point of ash.

Figure 1 has been prepared by Mr. H. J. Rose to show the relation between the sulphur content of coal and the sulphur content of blast furnace coke made in a large number of by-product coke oven tests

on different coals. Although there is considerable variation, the general tendency is remarkably uniform. With coals containing from 0.5 to 3.0 per cent sulphur, the per cent sulphur in the furnace coke averages about 80 per cent of that in the coal. It must be emphasized, however, that this must be used only as a general average figure. The percentage in any specific case may be quite different.

Data relating to the proportions of sulphur retained in the coke and eliminated in the coking process were published by the writer<sup>16</sup> some years ago. In these figures, the percentage of the coal sulphur retained by the coke generally ranged between 50 and 65, but there were several cases in which the percentage retained was much higher—for example from 70 per cent to as high as 79.6 per cent.<sup>17</sup>

*Relation of Coal Sulphur to Coal Gas Purification.* It is the writer's opinion that apart from the question of coke quality, the most important consideration relating to sulphur in coals used for coal gas manufacture may prove to be one that is usually little heeded, viz., the limit at which the removal of organic sulphur becomes necessary. This consideration may be more important than the cost of removing hydrogen sulphide.

Notwithstanding the facts that the legal limit for organic sulphur is usually 30 grains per 100 cubic feet in the United States and that in Nova Scotia and England coal gas, with a somewhat higher content of organic sulphur, is distributed, there is every reason to believe that the gas industry in the United States would require removal of organic sulphur at a point well below the legal limit. This point might be in the neighborhood of 25 grains per 100 cubic feet.<sup>18</sup> This would mean that a coal gas company facing the prospect of using coal containing 1.75 to 2.00 per cent of sulphur might have to install equipment for partial removal of the organic sulphur. An increase of 1 per cent of sulphur in the coal effects an increase of about 380 grains of  $H_2S$  per 100 cubic feet of the gas. Assuming a yield of 11,000 cubic feet of gas per net ton of coal, the increased cost of hydrogen sulphide removal due to the higher sulphur content of the coal would be about 1.33 cents per 1000 cubic feet or about 14.6 cents per ton coal. If the Seaboard Process could be used the

<sup>16</sup> Jour. Franklin Inst., August, 1918, p. 133.

<sup>17</sup> See also the studies made by S. W. Parr and A. R. Powell, particularly Jour. Ind. and Eng. Chem., November, 1920, p. 1069.

<sup>18</sup> Note the more rigid municipal regulations mentioned on page 44.

increased cost of purification would be only 0.38 cent per 1000 cubic feet or about 4.2 cents per ton coal. It may be assumed for purposes of comparison that coal washing costs 25 cents per ton of washed coal produced, including fixed charges. Therefore, from the standpoint of hydrogen sulphide alone, a company owning both city gas works and coal mines would find it cheaper to pay the increased costs of gas purification than to install coal washing equipment to reduce the coal sulphur from 2 to 1 per cent. If, however, such a company were obliged to resort to organic sulphur removal as a consequence of its use of the 2 per cent sulphur coal, this would immediately impose an additional burden amounting to not less than 1.5 cents per 1000 cubic feet of gas or 16.5 cents per ton of coal and perhaps even more,<sup>19</sup> so that the total increase in the cost of purification would be from 21 cents to over 31 cents per ton depending upon the processes employed.

The example just discussed assumes that the sulphur in the coal under consideration can actually be reduced from 2 to 1 per cent by washing. From the standpoint of coal washing practice, this would be quite a radical reduction and one that could not be obtained with the majority of coals.

Considering coals containing more than 2 per cent of sulphur, the possibilities of the Seaboard Process in conjunction with organic sulphur removal become more and more important. This process is capable of dealing with large increases of hydrogen sulphide at comparatively small additional costs and within all probable limits of sulphur that would have to be considered by a gas company, this process would appear to make gas purification cheaper than coal washing, with the all important but exceptional assumption that the coke from the higher sulphur coal could be sold at the same price as that from the lower sulphur coal.

Similar considerations, of course, apply in the substitution of a cheaper coal of higher sulphur content for a more expensive coal of lower sulphur content, but the very approximate nature of the figures used for such calculations must again be emphasized in this connection.

The writer's personal opinion of the sulphur question in connection with the manufacture of coal gas may be summed up as follows:

Where coke quality is important, particularly in plants producing

<sup>19</sup> The recovery of benzol from gas effects a substantial reduction of organic sulphur and where conditions are favorable to such recovery, these calculations must be made on a different basis.

metallurgical coke or in highly competitive situations affecting water gas and domestic coke, the use of low-sulphur coals should be regarded as a necessity irrespective of any consideration of gas purification.

In situations where the effect of sulphur on the value of the coke may be disregarded, it may be cheaper to pay the increased costs of gas purification rather than to undertake coal washing. The critical point is that at which the removal of organic sulphur becomes necessary, which may be between 1.75 per cent and 2.00 per cent of sulphur in the coal. At this point the increased cost of purification may be about equivalent to the cost of coal washing unless the Seaboard Process can be used for removing the hydrogen sulphide. This process is the cheapest method so far developed for dealing with large amounts of hydrogen sulphide, and its application in conjunction with organic sulphur removal may be cheaper than coal washing within all limits that are likely to be considered.

### WATER GAS

Most water gas manufactured for city distribution is in the form of carburetted water gas. The sulphur in this gas originates not only from the generator fuel, but also from the carburetting oil. It will, therefore, simplify our present study if we consider the sulphur distribution in blue water gas in which no oil is used.

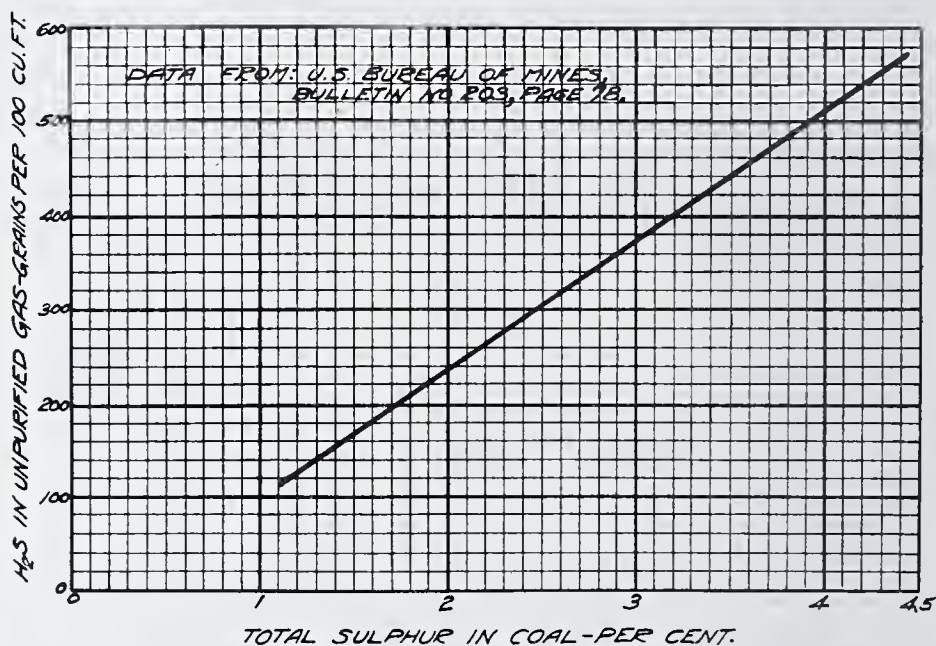
The best data on this subject are to be found in the investigations of the Institution of Gas Engineers in England.<sup>20</sup> In these investigations, coke was used containing 1.7 to 2.1 per cent of sulphur. The hydrogen sulphide averaged 287 grains per 100 cubic feet in one series of tests, but was substantially lower in a later series (approximately 200 grains per 100 cubic feet).

Consideration of these reports and other information would indicate that about 45 per cent of the sulphur in the coke goes into the blue water gas. The coke consumption per thousand cubic feet of blue water gas naturally varies with a variety of conditions, but a figure of 40 pounds per thousand cubic feet may be taken as typical. Thus a coke containing 1 per cent of sulphur might be expected to produce a gas containing 134 grains of  $H_2S$  per 100 cubic feet, while a

<sup>20</sup> See particularly the 6th and 10th Reports of the Research Sub-Committee of the Gas Investigation Committee on the Manufacture of Blue Water Gas (Gas Journal, June 15, 1921, p. 619, and July 4, 1923, p. 134).

coke containing 2 per cent of sulphur would produce a gas containing 268 grains per 100 cubic feet.

This same figure of 45 per cent also appears to apply to the sulphur in water gas made from bituminous coal. Figure 2 is reproduced from Bulletin 203 of the United States Bureau of Mines. It shows an increase of about 140 grains of  $H_2S$  per 100 cubic feet for each 1 per cent of sulphur in the coal. The tests were made on carburetted water gas, but as the same oil was presumably used throughout, the effect shown in the increase of hydrogen sulphide is due entirely



RELATION OF TOTAL SULPHUR IN COAL TO HYDROGEN  
SULPHIDE IN UNPURIFIED CARBURETED WATER GAS.

FIG. 2.

to the increase of sulphur in the coal. About 42 pounds of bituminous coal was taken as the average amount required to produce 1000 cubic feet of carburetted water gas in these tests so that about 45 per cent of the increase in the coal sulphur appeared in the gas as hydrogen sulphide.

There is not much information as to the relation between coal sulphur and organic sulphur in water gas. Most of the water gas produced in the United States is made from low-sulphur fuel and contains little organic sulphur. In the tests made in England the organic sulphur was quite irregular, but averaged 22 grains per 100

cubic feet in one series. It is probable that within ordinary limits about 4 per cent of the sulphur in the coal appears as organic sulphur in the water gas.

In order to calculate roughly the effect of an increase in coal sulphur on the cost of purifying water gas, let us take the Bureau of Mines figures for the manufacture of carburetted water gas from bituminous coal, and assume the yield of 47,800 cubic feet of carburetted water gas per net ton of coal. For an increase of 1 per cent in the coal sulphur, the increased cost of hydrogen sulphide removal by the Seaboard Process would be  $47.8 \times 1.4 \times 0.1 = 6.7$  cents per net ton of coal. The increased cost of gas purification by the other processes would be  $3\frac{1}{2}$  times this amount or 23.5 cents per net ton of coal. Coal washing would, therefore, have to effect a reduction of more than 1 per cent to be profitable from the standpoint of sulphur alone. However, the possibilities of reducing the percentage of ash and increasing the fusing point of the ash must always be taken into consideration in deciding any specific case.

#### PRODUCER GAS

Tests made by The Koppers Company Laboratories on producer gas made from Pittsburgh coal containing 1.5 per cent sulphur showed 105 grains hydrogen sulphide and 20 grains organic sulphur per 100 cubic feet. Similar tests of producer gas made from coke give the following results:

PER CENT SULPHUR IN COKE	ORGANIC SULPHUR	H <sub>2</sub> S
	<i>grains per 100 cubic feet</i>	<i>grains per 100 cubic feet</i>
0.71	8.3	60
0.62	8.6	40

Tupper's statement, cited by Crabtree and Powell,<sup>21</sup> that producer gas made from Westmoreland coal containing 1.5 per cent sulphur will contain 720 grains of H<sub>2</sub>S per 100 cubic feet, must be seriously in error and cannot be reconciled with his claim that about 40 per cent of the sulphur in the coal passes into the gas produced from it.

Rambush<sup>22</sup> states that tests have been made on large gas producer plants using bituminous coals, which show that between 70 and 90

<sup>21</sup> Transactions of the American Institute of Mining and Metallurgical Engineers, 1920, p. 718.

<sup>22</sup> Modern Gas Producers, 1923, p. 115.

per cent of the total sulphur in the coal remains in the crude gas leaving the producer as hydrogen sulphide and that no sulphur is present as sulphur dioxide. The lower figure is corroborated by the above tests made in our laboratories. In the case of the coal producer gas, assuming a yield of 140,000 cubic feet of producer gas per ton of coal, about 70 per cent of the coal sulphur appeared as  $H_2S$ . Rambush, however, makes the further statement that about 40 to 50 per cent of this hydrogen sulphide is generally removed from the gas by the cooling water. This does not agree with our experience. A reduction of more than a few grains under ordinary cooling conditions would not be expected and has not been shown by any of our tests.

It is interesting to note that in the case of the producer gas made from coke, from 60 to 80 per cent of the sulphur was evolved as  $H_2S$ .

*Purification of Producer Gas.* Until very recently, the removal of hydrogen sulphide from producer gas has received little attention. Dry purification is impracticable in most cases on account of the large expense involved. The size of the purifier boxes calculated not in terms of gas volume but in terms of heat units is very large in comparison with the equipment required for coal gas purification and the disadvantages are augmented by the high specific gravity of the producer gas which requires increased pressure differentials and higher pumping costs or else very large box areas to obtain the same differentials.

The successful development of liquid purification has, however, opened new possibilities. The purification of producer gas can now be economically accomplished for several purposes by the Seaboard Process and there appear to be excellent possibilities for the application of the Sulphur Recovery Processes where the Seaboard Process cannot be employed.

*General Conditions for the Purification of Industrial Gases.* Hitherto this paper has dealt almost entirely with the problems of coal sulphur and gas purification as they affect the manufacture of gas for city purposes. The removal of sulphur from an industrial fuel gas, such as producer gas, involves the same technical principles, but there is one important point of essential difference. This difference lies in the fact that the requirements as to the amount of sulphur in the purified gas are much less rigid than in the case of city gas. In most cases, the organic sulphur may be disregarded and a removal of 85 per cent of the hydrogen sulphide is entirely satisfactory. This means that a low-cost process, such as the Seaboard Process, may be

applied without any necessity for auxiliary equipment to remove the last traces of hydrogen sulphide. It also means that the Sulphur Recovery Processes can be substantially cheapened.

In the case of producer gas generally, some idea as to the allowable limits for sulphur may be gained by considering specifications for gas producer coal. In the absence of means for direct purification of the gas, such specifications have been the only method of controlling the amount of sulphur in the gas. For uses such as glass manufacture, open hearth steel manufacture, heating and reheating of steel for various purposes, the manufacture of certain refractory materials, etc. a low sulphur coal is always insisted upon. If the coal is to be used for making gas for open hearth steel manufacture, the sulphur should not be above 1 per cent.<sup>23</sup> This same limit is imposed or should be imposed in many other industries where producer gas is used and in certain cases it would be desirable to have a lower limit. Assuming that 140,000 cubic feet of gas are purified per ton of coal and that 70 per cent of the coal sulphur appears as hydrogen sulphide in the gas, this would mean that the producer gas should contain not more than 75 grains of  $H_2S$  per 100 cubic feet.

*Industrial Application of Gas Purification.* Several liquid purification plants have recently been installed in Europe for the removal of hydrogen sulphide from producer gas used in glass making. It is understood that any considerable amount of sulphur is particularly objectionable in certain phases of manufacturing glass—particularly in the gas used in glass machine operation, preparation of finished articles, etc.

A very important application of gas purification has been in connection with the manufacture of open-hearth steel. Hitherto, this has affected producer gas only indirectly. For example, one large steel company is using the Seaboard Process for the removal of 85 to 90 per cent of the hydrogen sulphide from the surplus gas produced by its by-product coke ovens. This low-sulphur coke oven gas is then used in conjunction with producer gas in its open-hearth furnaces and makes possible the use of a higher sulphur coal and therefore a cheaper coal in the gas producers.

However, the primary reasons for advocating the purification of fuel gas for open-hearth steel manufacture are not usually the possibilities of using coal of higher sulphur content, but they consist in the

<sup>23</sup> Producer gas as an industrial fuel, D. J. Demorest, Chem. and Met. Eng., October 13, 1924, p. 578.

direct lowering of the cost of making open-hearth steel, the possible reduction of the cost of blast furnace operation, the improvement in the quality of the steel produced, and the practical elimination of off-grade steel. This subject has been extensively studied and discussed both in this country and in Europe. Particular reference should be made to the papers published by A. N. Diehl<sup>24</sup> and by C. H. Herty, Jr.<sup>25</sup> The subject was discussed by the writer<sup>26</sup> before the Eastern States Blast Furnace and Coke Oven Association, June 4, 1925. Two steel plants are now operating on a purified gas and the near future will undoubtedly see a large number of purification plants installed primarily for open-hearth steel gas. The increasing production of alloy steels and the tendency toward more rigid specifications in ordinary grades of steel will make the removal of sulphur more and more a necessity.

There are a number of other applications where the purification of producer gas or other gas manufactured primarily for industrial purposes should be advantageous. Mention might be made of the difficulties found in using high sulphur gas for burning red face brick, sewer pipe, and other ceramic materials.<sup>27</sup>

*Cost Considerations in the Purification of Producer Gas.* Full consideration of the economic questions involved in the purification of producer gas would require a separate paper. Only a few of the more important points can be discussed here. First of all, in order to apply existing methods to the removal of hydrogen sulphide from producer gas, the gas must be cooled. This involves equipment for water scrubbing and tar removal. It also requires that the furnaces be equipped with producer gas regenerators which are not necessary when the hot, raw producer gas is used.

In this connection, the use of coke instead of coal for making producer gas should always be considered where low sulphur is desirable.

<sup>24</sup> Action of sulphur in basic open-hearth steel practice, A. N. Diehl, Year Book of the American Iron and Steel Institute, 1926, p. 404.

<sup>25</sup> Absorption of sulphur during melting in the open-hearth furnace, C. H. Herty, Jr., Mining and Met., October, 1926, p. 444.

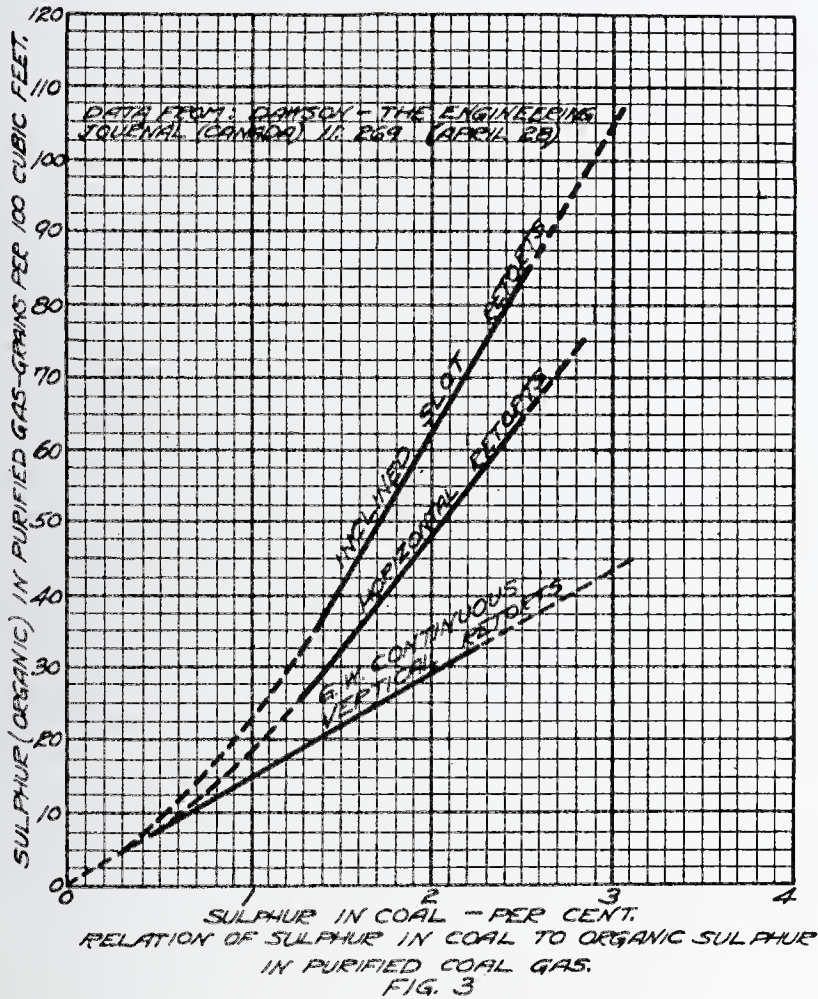
Some factors affecting the elimination of sulphur in the basic open-hearth process, Trans. Amer. Inst. Min. and Met. Eng., 1925, p. 513. See also Absorption of sulphur from the fuel gases in the open-hearth furnace, A. Jung, Stahl u. Eisen, 1924, p. 911.

<sup>26</sup> The purification of open-hearth fuel gas, F. W. Sperr, Jr., published by The Koppers Company, Pittsburgh, Pa.

<sup>27</sup> Fuels and Furnaces, March, 1928, p. 370.

A large amount of sulphur is eliminated in the coking process and the coke is a cleaner and easier fuel to handle. It produces a gas practically free from tar which requires a very simple water scrubbing operation to cool it and remove suspended solid material.

In comparing the relative economies of removing sulphur by coal washing or by application of liquid purification to producer gas made



from unwashed coal, the principal question is the efficiency of the coal washing process. It is quite obvious that coal washing will be much the cheaper method where it can accomplish a reduction of the coal sulphur to 1 per cent or less. The cost of the Seaboard Process applied for the removal of hydrogen sulphide from producer gas made from coal containing 2 per cent of sulphur might be as low as 0.4

cent per 1000 cubic feet, but with the production of 140,000 cubic feet of producer gas per ton of coal this would mean 56 cents per ton of coal and the cost of cooling and tar removal, would considerably increase this figure. However, many coals containing from 1 to 2 per cent of sulphur cannot be washed with the requisite efficiency. Most coals containing more than 2 per cent of sulphur could not be washed so as to make satisfactory gas producer fuel. There are many cases where such coals can be obtained at sufficiently low cost to warrant their use for the manufacture of producer gas from which the hydrogen sulphide is removed by liquid purification.

### DISCUSSION

EDGAR STANSFIELD (Scientific and Industrial Research Council of Alberta, Edmonton, Canada): Three weeks ago, through the courtesy of Dr. Lessing, I visited his plant which is about 30 miles from Swansea. As unfortunately Dr. Lessing is not here, it is almost my duty to give some of my impressions of that plant.

It is a small plant, the figures given are two tons of coal an hour. At the time of my visit it was washing anthracite coal, very fine anthracite coal. It appeared to me that the coal they are washing is a much easier proposition than most of the coals that I have seen washed in other places. At the same time I would like to state how favorably impressed I was with the cleanliness of the plant and the simplicity and smoothness with which everything was working.

When Dr. Lessing first told me he was adopting flotation on calcium chloride solution I thought that it was a pipe dream. I confess that I had to change my opinion when I saw the plant in actual operation.

In the paper Dr. Lessing emphasizes clearly the first feature, that of the necessity for the complete removal of the dust. Whilst hearing Dr. Fieldner read it I was not sure whether the second point, as to the method of washing the solution of the coal, was equally clear. If the solution is allowed to drain off the coal in the vertical draining tanks, and the coal then washed with water, a lot of water is required and a large quantity of dilute solution results which has either to be concentrated or wasted. He has adopted an ingenious process. Water is gently run in on the top while the tank is still filled with calcium chloride solution. As the solution is then run out from the bottom, the line of separation travels down through the tank without much mixing. The coal is very completely washed in a short time and only a little intermediate strength solution which has to be concentrated is produced.

That reminds me of the question of concentration. He referred to using washery refuse as his fuel for concentrating that solution. I think his tables showed the small amount of coal that was left in the refuse. It would be unfair to his washing plant to assume that it was his own washery refuse he was burning; that contains too little coal to be worth burning, so he uses the washery refuse from another plant in the vicinity.

W. H. LESSER (Madeira Hill & Company, Fraeville, Pa.): I would like to ask the gentleman the specific gravity of the coal and the specific gravity of the slate in the anthracite coal.

MR. STANSFIELD: I am afraid I can not answer that without looking at my notes.

G. R. DELAMATER (Fuel Engineer, The W. S. Tyler Company, Cleveland, Ohio): Calcium chloride, I believe, can only be made up to specific gravity of about 1.40 or if kept hot, to 1.43. With many of the coals in this country we have to use a specific gravity above that, possibly 1.45 to 1.60.

Many of you know my connection with the float and sink test. In my work I use zinc chloride almost entirely. With our anthracite coals in this country I think if I am not mistaken you have to use a specific gravity of 1.75 to 1.80. The process described, is very interesting and if we can find a liquid cheap enough that we can get a specific gravity from 1.45 to 1.75 then I think we can use it.

Mr. J. R. Campbell, I remember, about 10 or 12 years ago experimented right here in the Pittsburgh district with calcium chloride. He had a machine that he used, I think, for several months, making separations of bituminous coal. He found he would have to use a higher specific gravity than 1.40 on our coal.

I would be interested in knowing what they found in England with regard to the gravity, whether they can do all they want at 1.40 and less.

He quotes figures as to the quantity of calcium chloride left in the coal. I was not clear, in hearing that paper, as to whether that was the figure he obtained with the anthracite coal or whether he also included figures for softer coal. I confess that I would personally like to know how much was left with some of the other coals he treated and how much would be left in the coal or lost in the rinsing with some of our more friable coals. It appears to me that is a most important point as to whether the loss of solution with friable coal would be greater than it is with the anthracite coal.

JOHN V. FREEMAN (United States Steel Corporation, 71 Broadway, New York, N. Y.): I just want to have this figure verified. I understood that the consumption of calcium chloride was at the rate of half a gallon per ton of coal. That is to say, you have to add the new chloride at that rate, is that correct, half a gallon to a ton?

MR. STANSFIELD: I think in one case he said 2 gallons.

MR. LESSER: I have half a gallon.

MR. STANSFIELD: He told me 2 or 3 liters. The figures given by Dr. Lesser are liable to be misunderstood. They are sometimes based on the ton of raw coal received, not on the ton of dust free coal put through the washing process.

CHARLES ENZIAN (The Berwind-White Coal Mining Company, Windber, Pa.): I do not know whether I got here in time to learn whether Mr. Fieldner covered the point or not, but Dr. Glinz mentioned the practicability of coal cleaning as it is reflected in additional market price, or commercial value to the cleaning company of the various kinds of coal. In the words of Dr. Sperr is it worth while, does the operating company that incurs the expense of cleaning coal get a higher price, or sufficiently increased price, over the ordinary market to justify the expense? I am fairly familiar with the results in this state but it would be interesting to know whether they have realized that position abroad?

MR. STANSFIELD: Coal purification is going ahead very rapidly in England. I think this proves it to be economically sound there at any rate.

H. L. RICHARDSON (West Kentucky Coal Company, Paducah, Ky.): I have made a few tests recently in the pneumatic cleaning of western Kentucky high sulphur coals. While the results are not at all complete I have found a great deal of encouragement in consulting with purchasing agents as to being reimbursed for the cleaned coal to the extent of the cost of cleaning it, or more. I think in all probability we will find it possible to use either the pneumatic process or a combination of the hydro and pneumatic processes in these coals and will find a satisfactory return when the coal is marketed.

CHAIRMAN STEIDLE: Is there a discussion of Dr. Glinz' paper?

JAMES A. YOUNKINS (Research Fellow, Bureau of Mines, Pittsburgh, Pa.): How accurate is the separation of fusain from coal—what percentage?

DR. GLINZ: The recovery is more for fusain than for the vitrain. The fusain is much more cleaned than the vitrain.

MR. YOUNKINS: Do you separate 85 per cent of fusain from coal with no mixtures?

DR. GLINZ: In the case of the sludge that contains 40 per cent of fusain and 30 per cent vitrain. In employing woven sieves you get 55 per cent fusain and 23 per cent vitrain. In using slit-screens you get 75 per cent fusain and 12 per cent vitrain.

CHAIRMAN STEIDLE: Is there a further discussion of this paper?  
If not, we will take up Mr. Sperr's paper.

MR. FREEMAN: Doctor Glinz stated he found that the centrifugal dryer acted in the dual capacity of an ash extractor. To what extent does it do that? Is it qualitative only, or is it a real appreciable value in the removal of ash?

MR. DELAMATER: He referred to clay or materials of that kind as I understood it. It was more or less dissolved.

MR. FREEMAN: What percentage?

MR. DELAMATER: In most coal it would not amount to anything.

DR. GLINZ: The removal of dissolved clay with the hurled out water is an agreeable accompaniment of centrifugal action. The reduction of the percentage of ash to a considerable extent is, however, impossible in this manner.

CHAIRMAN STEIDLE: Is there any discussion of Mr. Sperr's paper?

MR. ENZIAN: I would like to ask Mr. Sperr a question. When you speak of total sulphur in coal, or speaking of per cent of sulphur in coal, you mean the total sulphur?

MR. SPERR: I mean the total sulphur, yes sir.

M. P. KANGA (Perry Iron Company, Erie, Pa.): What per cent of oxygen or air do you need to have in a coke oven gas to give the most efficient purification in ordinary box purifiers?

MR. SPERR: The theoretical percentage is very low, but in practice one has to use an excess. I do not know what is the most efficient percentage. In usual practice sufficient oxygen is added to make the total oxygen in the gas somewhere around 1 per cent. Remember that this is America and that our gas is low in sulphur.

RALPH L. DODGE (Lazote Incorporated, Wilmington, Del.): In connection with your mention of the use of pressure scrubbing in the treatment of gas, have you found any particular advantage, such as a reduced volume of solution, that would be employed that would offset the increase in cost of the pressure of the gas, or was that in connection with high pressure delivery of gas?

MR. SPERR: The answer to that is that it is not economical to compress the gas merely for purification. The point is we have to purify a great many gases which are already under high pressure, such as natural gas for example, or where the location of the purification plant is most advantageous to purify manufactured gas under high pressure. It is not economical to compress the gas merely for the sake of purification. We find that in our high pressure plants, and by this I mean the efficiency obtained with a single absorber. That is perfectly natural because the rate of absorption should increase with the pressure.

HORACE C. PORTER (Consulting Engineer, Philadelphia, Pa.): Mr. Sperr has given us most valuable data on the purification of coal and of gas and the relations between them as it applies to that portion of our coal that is made into the gas. He looks at this thing from the standpoint of the gas man and the production of gas from coal.

Both Mr. Sperr and I would like to see all of the coal, if it were possible,

converted into coke and gas and by-products before being used. But statistics show that about 70 per cent now is not converted into gas but is burned direct. So how does this question work out as to that 70 per cent? Some day the consumers are going to demand that we have less sulphur in our steam coal. We should not send so much sulphur dioxide out into the atmosphere. It corrodes structural steel work and is injurious to the public health.

I believe coal cleaning is going to be applied some day to the reducing of sulphur in all of the high sulphur coal, as used for any and all purposes, and the economics of that problem would be interesting to work out.

LESLIE R. THOMSON (Consulting Engineer, Montreal, Canada): In regard to Mr. Sperr's last remarks about reduction of sulphur and ash by washing, the approximate figures in Nova Scotia would be as follows: If the coal goes into the washer at, say 3.5 per cent sulphur it usually comes out at about 3 per cent sulphur, representing a gain of 0.5 per cent. The corresponding figure for the ash would be a gain of about 2.5 per cent, and the other washings would run from 8 to 11 or 11.5 per cent. All the coal and coke is washed, of course.

MR. ENZIAN: In answer to Mr. Porter's question to Mr. Sperr, and to Mr. Sperr's answer; from two years of practical experience in cleaning coal in a dry cleaning plant, and about five years in study of flotation—we can substantiate his comment. The ash reduction in bituminous coal, as well as semi-bituminous coal, is very satisfactory. The sulphur reduction in bituminous coal is very much less than in semi-bituminous coal. In other words; in bituminous coal we can get a sulphur reduction of about 20 per cent, whereas in the semi-bituminous we can get as high as 35 per cent of sulphur reduction.

# THEORY OF WASHING AND WATER OR PNEUMATIC CLEANING

By A. FRANCE

*Inventor of Rheolaveur System of Coal Washing, Liege, Belgium*

*Read by James R. Campbell, Koppers-Rheolaveur Company, Pittsburgh, Pa.*

## THEORY OF WASHING

It can be said that all the theories of washing coal which have been thus far described lack pertinence because the authors of them generally analyzed only one phenomenon which was supposed to be required while the effects of this phenomenon are almost nil when combined with the effects of a large number of other phenomena, the laws of which are not known to us. Once understand that, a complete analysis of these combined phenomena having been made, the results remain entirely Utopian. It is then necessary to try to analyze the law of certain of these phenomena from which the observation made is essential in a process.

One of these essential phenomena that we try to realize in certain processes of washing, is the stratification (*Alluvionnement*) that is to say, natural classification in a flowing stream of water, which a Belgian engineer, Mr. R. Henry, has remarkably analyzed in a paper which was published in the *Revue Universelle des Mines*. The theory of this phenomenon that he gives, which is confirmed by experience, leads to the conclusion of the possibility of forming a deposit of material of all sizes of the same gravity by establishing a pitch, which he calls the pitch of *Alluvionnement*, or stratification, in which the angle of inclination above horizontal, depends only on the gravity of the material settled, this pitch being steeper when the material to be settled is heavier. It happens that when we run over this pitch a mixture of heavy and light material, the heavy product slides along the slope, while the light material floats over. This phenomenon is the fundamental principle of the Rheolaveur process, which is a process that realizes the separation by gravity in one launder, or several launders underneath the action of a current of water, where the extraction of all the heavy material which travels along the slope is made by means of apparatus with water currents. This apparatus is placed at greater or less intervals underneath the bottom of the

launder in which slots are provided and correlate with the compartment of the apparatus which is used for evacuation of the heavy material.

Before proceeding further with the particularities of the Rheolaveur process, we would like to draw attention to what have to be the steps in the washing of coal. The principles of the washing of the coal is the separation into two products, one being composed of particles having a low specific gravity and the other of particles having a higher specific gravity at one determined specific gravity. It happens as a general rule that the ash content of the particles of coal and the shale are in direct proportion to the gravity. We can then say with a certain exactitude that the washing makes the separation into two products, one having a low ash content and the other a high ash content. This analogy is sometimes misleading to the owner of the coal washery, because his attention is directed only to the ash content of his own product, and he misunderstands the technical object of the washing operation from which comes the false conception of the efficiency of different processes of washing. This separation at a given specific gravity of washing, is perfectly illustrated by the washability curves, the first idea of which came from a French engineer, Mr. Chavet, and the value of these curves was particularly illustrated by Mr. R. Henry, who has been mentioned before in a paper that he has published in the *Revue Universelle des Mines* from Liege.

We, ourselves, have generalized the use of washability curves as the basis of our advertising of our process of washing and also by using it for the washer performance. On the same basis, it was introduced by the Rheolaveur Corporation in the United States several years ago, where it is now used almost as a universal language in coal washing, and we do not think it is necessary to speak further about this phase of the subject. The theoretical problem is then to make a separation at a given specific gravity. The practical problem is to make this separation as complete as possible; therefore the most efficient washing process is the one that will produce washed coal with a minimum sink and refuse with a minimum float at the predetermined specific gravity. We want to emphasize particularly this point of view against the belief in several countries that the determination of practically pure coal floating in the refuse and practically pure refuse sinking in the washed coal, is sufficient to appraise the efficiency of a process. Only the making of washability

curves on both ends, refuse and washed coal, will allow us to calculate the accuracy of the separation.

These considerations lead us to say that the guarantee of washery builders, when they say that the ash in the washed coal will not be more than 2 per cent above the fixed ash, is an appraisal that we classify as childish.

What is the fixed ash? In certain countries where this formula is very much used, it is considered at once that the fixed ash is the ash content of the particles with a specific gravity of 1.5. This notion seems to us completely arbitrary, and we do not know the reason for it.

The best washing process is the one that gives to its owner a washed coal of any ash content imposed by the market conditions, if, naturally, the nature of the coal indicates the practical possibility of doing it. The problem is not any more, if it ever was, the question of getting the cleanest coal possible with a reasonable recovery, but it is to have clean coal which will meet all the market conditions. These market conditions will vary and it is necessary to have coal which will suit the best market conditions.

It is necessary to know the complete possibility which can be given by a washing plant, the nature of the coal that we have to wash, and follow very closely the market variations.

We want to add a few words concerning the recovery and efficiency of a washing plant. Almost all the writers who have described the theory of coal washing, have deduced the theoretical recovery of a washing plant from the following formula, which expresses what the ash in the raw coal is equal to ash in washed coal and ash in the refuse.

$R$  = Recovery.

$C_b$  = ash in raw coal.

$C_1$  = ash in washed coal.

$C_p$  = ash in refuse.

$$R \times C_1 + (1 - R) C_p = C_b$$

$$R = \frac{C_p + C_b}{C_p - C_1}$$

In a general way, it is called practical recovery, the ratio between the weights of the washed coal and the corresponding raw coal. It

is a mistaken conception to compare the efficiency of two washing plants treating coal quite different, based on their recovery as defined above. This recovery is not at all the one which comes from the washery. It simply shows the recovery of coal of a determined nature by the washing operation and by the process considered, and this is more so when the nature of the raw coal has a greater influence on this recovery than the efficiency of the washing plant itself. The true efficiency of a washing plant is the relation between what we call practical recovery and its theoretical recovery, which is that recovery shown by the washability curves made by heavy density liquids for a determined ash content and a determined case, and for which the formula is as follows:

$$R = \frac{C_p + C_b}{C_p - C_l}$$

Practical recovery is the result of the washing. Its formula is as follows:

$$R' = \frac{C'_p + C_b}{C'_p - C'_l}$$

The measure of efficiency of a washer is then given by the following ratio:  $R'' = \frac{R'}{R}$ .

We now come to the description of the phenomenon as they occur in the washing of coal by the Rheolaveur process. As we said above, the washing has to make a separation by gravity. It has been noted and copied that the natural phenomenon of Alluvionnement from which a stream of water carrying a mineral, permits a settling of the heavier product after a certain time, while the lighter product is floated further on. It is superior to all processes for the treatment of minerals where the products have a very wide range of gravities, and it was in this use that simple arrangements permitted the realization of this phenomenon.

It is now positively known that a body of coal falling in water in the beginning of fall, reaches a certain velocity which is in direct and exclusive relation to specific gravity and independent of volume. It can be easily understood that if the particles are disseminated along a launder, and disassociated from each other by the action of a stream of water, the heavy particles will reach the bottom of the launder quicker than the lighter ones which reach, consequently,

the last zone of the stream. Naturally, the thin heavy particles which are momentarily lost in the mass, rather than the big pieces, have a tendency to fall into the voids beneath them and after a sufficient length of time, all the heavy particles are traveling below the lighter particles. It is really surprising with what rapidity this is accomplished. We have found the reason for this phenomenon in the following peculiarities:

The speed of the stream is extremely variable in depth and nil when it comes in contact with the bottom of the launder with the maximum velocity at the surface. This phenomenon is particularly favorable for obtaining the results that we desire.

Under the action of the speed of the current in a cross section, the lighter particles travel faster than the heavier particles of same size and shape. The heavy particles have already a tendency to fall faster than the light particles. They will positively reach the bottom of the launder after a short travel. If the shape of the particles in question is flat for the refuse and cubic for the coal, the action of the stream on one and the other, increases considerably the difference in the velocity of fall. While the slate is under an extremely reduced action of the stream which makes it slide horizontally with a velocity retarded again by the effects of the mass, the particles of coal, on account of the cubical form, are drawn along by the current of different speeds which has the effect of making them roll and pass over the slate, and the larger the pieces are, the more they are affected by this favorable phenomenon, which separates them very quickly from the shale.

In order to accomplish rapidly and efficiently this separation, the arrangement of the trough, its pitch, its width, the form of its cross section, the form of the longitudinal section in the bottom, the speed of the stream, all of these have to be determined for each special case. This separation is only for a preparatory operation for the Alluvionnement. It constitutes, as we said above, the formation of a fixed bed which offers the peculiarity of presenting a constant inclined surface. Above this bed slide the heavy particles having a determined gravity traveling along with the stream of water, while the lighter particles are separated.

The formation of this stratification is obtained by a sharp reduction in the slope of the launder at the point where we want to realize it and by the use of barrages which have for the exclusive object, the acceleration of the formation of the deposit. The establishment of

the slope of Alluvionnement has very practical and particularly favorable results. The adherence given to the refuse sliding upon the fixed bed which has a rough and uneven surface, lowers considerably their motion, giving by so doing, the formation of a bed relatively thick and compact, because it is composed of heavy particles of all shapes and sizes. The extraction of this pure refuse seems to be a very simple problem. A variable opening in the launder will be sufficient if at the time of separation the water did not go with it. This water will cause suction in the launder which will have the effect of allowing the fall of light particles with the refuse. It is then necessary to prevent the water falling through the slots, and the means which we use, consists of maintaining underneath the slots, a water pressure which will permit the fall of the refuse, while the falling of the water through the slots is balanced.

These results are obtained by using a box with two compartments. In one of them we cause the introduction of the water under pressure and the other communicates with the slot in the bottom of the launder.

The evacuation of the refuse falling into the boxes is accomplished by several arrangements which depend upon the size of the particles handled. We think that these arrangements are well enough known and that it is not necessary to speak further about them.

On account of the impossibility of realizing a regular feed corresponding to an extraction of the pure refuse with a constant discharge, we were obliged to find a way to avoid the passage of the coal with the refuse, while the quantity of same is decreasing. We reach these results by introducing an upward current of water into the extracting compartment of the apparatus. Of course, this counter-flow is very light and its purpose is to elevate a little, the light products into the launder in order to help them to pass over the slot. It is a mistake to think that this current of water is for the purpose of sending back into the launder the small light particles which would have been carried with the refuse. Consequently, its velocity can be reduced until it is almost imperceptible and permitting, by so doing, the extraction of the finest particle of slate. In view of the evacuation of the very thin shale, we make a suitable regulation of the opening of the evacuation box to give to the heavy mud a certain compactness in such a condition that all the currents of water into the box can be suppressed.

This is the principle used in our silt washing plant with which we

are now making the complete washing of particles as small as 0.1 mm. By means of the influence of the mass, the phenomenon of Alluvionnement does not realize a complete separation of the small particles and the particles of intermediate gravity, until after a sufficient length of time and travel.

In order to reduce the length of the washing plant and to have a perfect separation, instead of expecting to carry away the large heavy particles by separating them completely from the lighter particles, we carry them away entirely without taking into account their purity and we send this material back with the feed to be rewashed. The coal generally contains a more or less important proportion of particles of intermediate gravity, and as the fine particles travel along the bottom of the launder, the material to be rewashed will be almost completely composed of very thin products and bone helping greatly the efficiency of the separation. This product gets into the interstices of the refuse and stuffs them and furthermore, realizing with the bone an artificial barrier more or less thick, between the refuse and the coal in order to render impossible the passage of pure coal into the refuse. This method in use in our process of washing, gives us a regulating product which corrects remarkably, all feeding irregularities and helps at the same time, the separation of particles in which the difference of gravity is only 0.10 or 0.20. The same method when used by the builders of other washing processes, such as dry cleaning, cannot obtain such good results. This is also true of the jig washer. The reason for this is that in the Rheolaveur process the effect of a horizontal current of water loosens up the mass of particles and leaves them free for an easy classification. The introduction into the raw coal of a large proportion of material of intermediate gravity, brings into the washing apparatus of other processes, the formation of a very thick bed of this material which will reduce the "setzage" or jiggling effect in the jig, or will reduce greatly the possibility of separation in the dry cleaning process, because the thickness of the bed on the table must have a very large influence which cannot be corrected by an air current in which the increased velocity is an opponent to the settling of the fine heavy particles. In consequence of this, in a jig and dry process it must result in the increasing of the ash content in the washed coal, if one does not lose too much marketable coal with the refuse.

I would be glad if this viewpoint of mine will be the subject of a discussion and that my own feeling in the matter will be practically checked from an operating standpoint.

This arrangement of ours in connection with our washing process has been described many times in technical papers and we beg our audience to refer to these papers for this matter.

We have reserved for this congress the exemplification of two new arrangements which seem to us very interesting. One of these arrangements consists in giving to the washing launder an appropriate

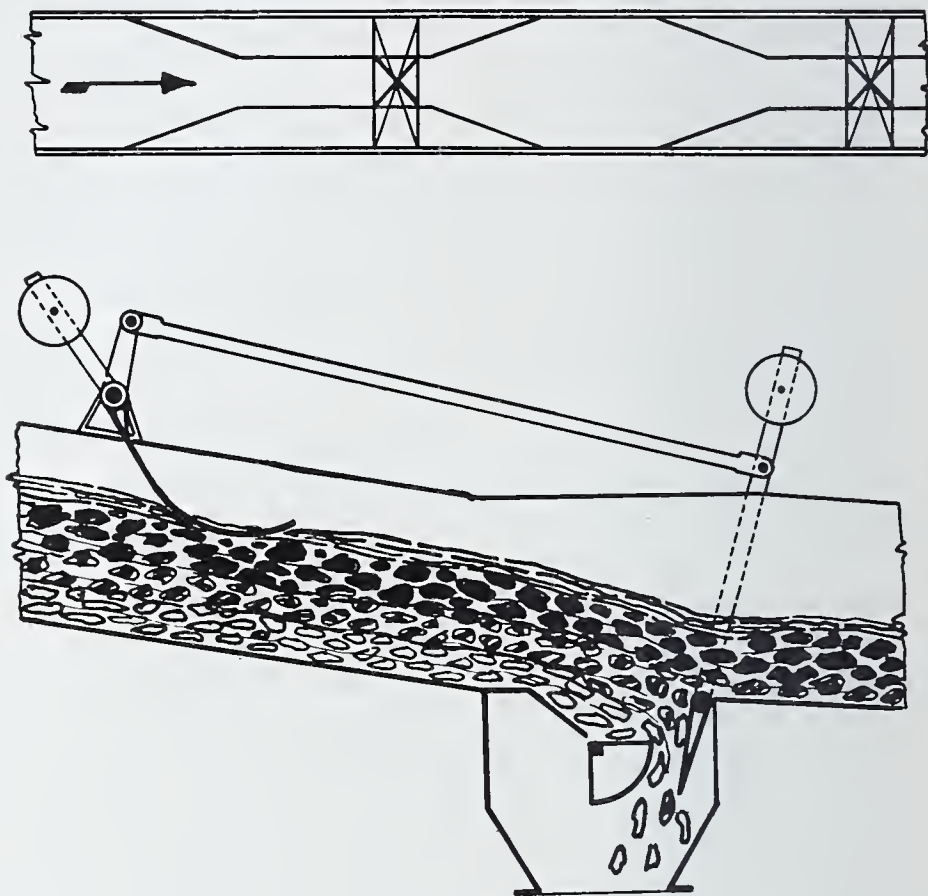


FIG. 1

longitudinal section in order to realize the succession of phenomena, the purpose of which is a perfect separation (see Figure 1).

The first part of this arrangement, the purpose of which is to prepare the Alluvionnements, is broad, permitting us to split the product under relatively small thicknesses. This will permit the heavy particles to reach immediately the bottom of the launder. Once this is reached, the launder becomes narrow in order to increase progressively the thickness of the bed of refuse without disturbing

the classification. The launder is now in a straight section at the point where the slope of Alluvionnement is formed, which gives the possibility of obtaining a bed of slate thick enough and the separation of the lightest products with a greater velocity to the water current. As it can happen that the counterflow water used in the box may elevate a few pieces of flat slate and a product of intermediate gravity into the lightest particles in the launder, we will split again the material upon a large surface by enlarging the launder, and we can have this launder made narrow again, if necessary, in order to have a new bed of refuse thick enough, and constitute a new slope of Alluvionnement ahead of the second Rheo Box which is the rewashing apparatus.

All these variations of the longitudinal section of the bottom of the launder described, can be combined with a cross section with flaring sides, and the possibility of regulation, if it is necessary, in order to put the washer in the best condition for the separation. The variation in the longitudinal section can be done by means of mobile partitions arranged in a launder of rectangular cross section.

The other sketch is an automatic regulator. It seems to us very interesting to use this because it is very simple. However, our washing plant is already automatic in itself. The float of this regulating apparatus moves with the variation of the pitch of Alluvionnement. The last one mentioned can be longer or smaller according to the variation of the refuse, while the pitch does not change. The float by its motion moves by the use of levers, a baffle inside the Rheo Box, closing or opening, more or less, the slope of evacuation of refuse according to the variation of the slope of Alluvionnement. This float can also very easily regulate the counter-flow into the boxes and the push current into the launders.

#### WATER OR PNEUMATIC CLEANING

In starting the second part of our paper we beg you to understand that it involves the general practice of coal cleaning and not only the practice of a country, as this Congress is international.

The advertisers of dry cleaning processes claim the following advantages:

- (1) To obtain fine dry coal
- (2) Elimination of drainage hoppers
- (3) Elimination of sludge
- (4) Transportation saving.

In order to make an intelligent comparison concerning the claims above, it is absolutely necessary to put dry processes and wet processes on the same basis. The dry cleaning process is inefficient for the particles below 0.5 mm. and it is not very efficient from 0.5 to 2 mm. Outside of this, the dust disturbs the washing efficiency of the top sizes, from which, as it is of current practice in other countries, it will be better to remove it by proper devices before washing. If we put ourselves in the same condition for wet washing and if we eliminate the 0 to 2 mm. which of course is not necessary, by washing the 2 by 8 mm., we can very easily dry it by means of very simple screens, and the moisture will not be higher than 8 to 10 per cent. If after that we store it in bins, we can after 24 hours, have the moisture as low as 5 per cent. The centrifugal driers now on the market can give the same moisture in a shorter way. It is surprising that thus far, this way of looking at the matter has not been opposed to the dry cleaning process. It is a general rule to compare the possibility of obtaining dry coal with the impossibility of obtaining washed coal with less than 10 per cent moisture, without showing that, with dry cleaning in order to get the results of washing comparable with the results of the wet cleaning, it is necessary to remove before washing the dust, 0 to 2 mm. We have shown that in the wet cleaning it is possible to obtain by simple means a product having a surface moisture of 4 to 5 per cent. The question then, is to know if 2 or 3 per cent extra surface moisture in the washed coal is a handicap in the wet cleaning.

It is a fact that it is very difficult to remove the dust, 0 to 2 mm. from the dry coal 0 to 10 mm. This is true in the wet process and in the dry process if you make this screening before washing and we would like to show the results in both processes with imperfect screening.

For the dry cleaning the results will be inefficient washing, which will depend upon the perfection of the removal of the dust and naturally, this removal will depend upon the amount of dust in the feed and also the degree of moisture. In the wet cleaning process by Rheolaveur, the inefficient removal of the dust is not important, and has no effect on the washing, which will be absolutely complete even if we have to wash the particles having more than 0.1 mm. It is a fact that the drying will be more laborious, but it can be done anyhow, and yet have a washed product with less than 5 per cent surface moisture, which moisture can be reduced by the mixing of this washed coal with the dry dust, 0 to 2 mm. It is a question if

one or two per cent more in the ash content of the products from the dry cleaning is of less value than a higher moisture of a few points. Whether or not it is an appreciable advantage to charge the coke ovens with dry coal having 2 or 3 per cent moisture against the use of coal having 4 or 5 per cent moisture, is very doubtful. In many cases and for peculiar coal, it is necessary to have a coal of 4 or 5 per cent moisture in order to obtain good coke. In facing this remark, the advertiser of the dry cleaning processes asserts that it is more advantageous to add the water where the coal is used. It is evidently a mistake because everybody knows the difficulty of having a uniform moisture by doing so, and especially taking into account that the product is very dusty, and in order to realize it, it would be necessary to have complicated installations. As a matter of fact, it is more advantageous to have a clean coal with low ash and with low sulphur content, and this question of the removal of sulphur is among the weak points of the dry cleaning process, and it is common knowledge, we believe, that no dry cleaning process can remove the sulphur with the same efficiency as the wet process, because the sulphur being among the fine particles, is blown into the dust hopper, and mixed with the clean coal afterwards in certain systems.

When we speak about the cleaning of the fine coal, it is because this size is the only interesting one to be dried. The question of washing above 10 mm. is not worth any discussion, because the wet washing for larger sizes is beyond the question of a doubt, more efficient than the dry cleaning process, no matter what the degree of moisture in the raw coal is, and also the handling of the big sizes along short or long tables will give a serious degradation; above all where the coal is very friable, and it will be very important to figure in dollars and cents what this means at the end of the year for a plant of average importance, making prepared sizes.

In the Rheolaveur process every point was carefully studied in order to eliminate degradation as much as possible, even for the most friable coal, and as said in the first part of the paper, the elevators are handling only refuse, bone and some fine coal, and everyone who has visited our plants has hardly found a large piece of coal in the elevator buckets.

In a cleaning plant when the type of table used requires air prescreening which, as we said above, ought to be of general practice at least for the removal of the dust, 0 to 2 mm., the fact is often overlooked that this prescreening gives an irregular division of the raw

coal to the different tables, and that these variations are noticeable on account of the variations in the nature of the raw coal which gives an uneven feeding to each table. It is then necessary to provide each of these, or at least the group of those treating the same size of coal, with a prestorage hopper. This also requires the frequent attention of the washer men, and we like to point out that when a washing plant depends upon the good-will of man, the efficiency of this same washing plant is yet a problem in itself. We would like also to bring to your attention the fact that the cost of these hoppers is often not less than the first cost of installing dewatering hoppers, which is the current practice in several countries.

Our experience in building these dewatering hoppers is that they cost only about one-tenth of the cost of the washing plant and thus afford an arrangement which can give 24 hours of dewatering. On the other hand, these dewatering hoppers are at the same time pre-loading storage bins of ample capacity, facilitating the loading of the washed coal in case of a shortage of railroad cars, and also, enabling a quicker loading. It is the general belief that the first cost of a complete dry cleaning plant from which can be expected a maximum of efficiency, is considerably higher than the first cost of a wet cleaning plant equipped for the same purpose, and, especially, when compared with a Rheolaveur washing plant of large capacity; the operating cost and maintenance of a dry table plant is also higher.

If you stop to think of it you will realize that only two operators are required for a Rheo plant, no matter what its hourly capacity is, and then figure how many men will be required for the same capacity plant equipped with tables.

Another fact which has to be considered is that the machinery and its character is more complicated in a dry cleaning plant which requires more care, horse-power and maintenance, while in the Rheolaveur process only few elevators are required and their construction is so carefully made that they last several years without giving trouble.

As pointed out above, the power required for a Rheolaveur washing plant, per se, including pumps, is lower than for any other process and  $\frac{3}{4}$  horse-power per ton, even  $\frac{1}{2}$  horse-power, is general practice. It is a serious mistake when comparing one process with another to include, as is the general rule, all the handling machinery outside of the washing process itself, in order to establish the amount of horse-power required.

Another advantage which favors the dry cleaning process is that the manufacturer of the process claims the elimination of sludge

handling which was at one time generally an expensive operation. At the present time, as we have several modern applications in this country, this conception of sludge handling is not true any more, because the handling of the sludge can be done in a very simple, mechanical way after being washed by the Rheolaveur process, which takes care of it in the same way as the larger sizes are taken care of. Consequently, it results in a larger recovery which means a lot of money each day for the coal operator. It is a fact that, as far as the dust is concerned, a great number of interested people have realized that it is more advantageous to handle the sludge in this way by wet processes than to produce dry dust which is uncleaned and loaded with sulphur; and, furthermore, the handling of dust is complicated.

The fact that the supply of water is sometimes difficult to obtain, seems to be a handicap for the wet process. However, we have plants handling as much as 500 tons per hour with drying devices for fine coal and sludge, which require only 150 gallons of make-up water per minute, and we ask you if such a small amount cannot be found anywhere, or brought to the washery at very low cost.

One of the other advantages claimed by the dry cleaning people is the saving in freight effected by shipping dry fine coal, which is of some importance, especially when the shipping point is far away from the destination of the coal, and that depends upon whether or not the railroad freight is paid by the operator or by the customer. While it is true for the bituminous fields of America, this point is of no value for the American anthracite, where water allowances are made on the smaller sizes. The same practice is in use abroad. We think that the American bituminous field will soon come to a satisfactory agreement on this subject, but in the meantime, the following paper by Mr. J. R. Campbell will show that this claim of the dry people is of very little moment if we examine the problem from a practical standpoint.

## MOISTURE VERSUS ASH

*By J. R. CAMPBELL*

*Bituminous Representative, American Rheolaveur Corporation*

*Problem:* (1) 6.5% ash + 3.5% moisture or  
(2) 8.0% ash + 2.0% moisture

Size coal, 4 inches by 1 inch, dewatered by natural drainage where 1% moisture = 0.7% ash, commercial use (0.65% German practice) and 1% moisture = 1% ash in freight hauls.

From a freight standpoint:

$$(1) 6.5\% + 3.5\% = 10.0\% \text{ total inerts}$$

$$(2) 8.0\% + 2.0\% = 10.0\% \text{ total inerts}$$

Therefore, the buyer of \$2.00 coal + \$2.00 freight, or \$4.00 coal is not penalized on the delivered price, but from a handling and using standpoint;

3.5% moisture is equivalent to  $3.5\% \times 0.7\% = 2.5\%$  ash and  $6.5\% + 2.5\% = 9.0\%$  total inerts.

2% moisture is equivalent to  $2.0\% \times 0.7\% = 1.4\%$  ash and  $8.0\% + 1.4\% = 9.4\%$  total inerts.

$9.4\% - 9.0\% = 0.4\%$   $\$4.00 \times 0.4\% = 1.6$  cents net saving to buyer on 6.5% ash coal with 3.5% moisture.

A further analysis of the problem shows that the buyer would not be penalized in any way if he bought coal with 6.7 per cent ash and 3.5 per cent moisture rather than coal with 8.0 per cent ash and 2.0 per cent moisture. From a highly technical standpoint there is about as much difference between the two cases as there is between tweedle-dee and tweedle-dum, but under all market and climatic conditions, there is the big difference between 8.0 per cent ash and 6.5 per cent ash or the difference between a "roughing job" and an efficient job, at a high washing gravity.

In handling 1 inch by 0 inch slack by the wet process, natural drainage may be used effectively on 1 inch by  $\frac{3}{8}$  inch and mechanical driers on  $\frac{3}{8}$  inches by 28 mesh, and mechanical filters on 28 mesh by 0, supplemented if necessary, by heat driers, in which case, the added moisture over the initial moisture may be 3.0 per cent. If only a "roughing job" is needed on slack coal 1 inch by 0 or  $\frac{1}{2}$  inch by 0 inch, dry processes may be used, especially in commercial work for a small reduction of ash content, but with an appreciable loss of coal in the refuse; but where the sulphur is a serious problem, wet processes must be used to attain the maximum removal.

Quality in metallurgical practice is the dominant factor and it must eventually be recognized in commercial work, as it costs money to handle ash in commercial and domestic uses as well as in blast furnace practice. This is brought out very clearly in "Fuel in Science and Practice" by Chapmann and Mott, English writers on the subject and it behooves us Americans to study the subject from more than a superficial and sales standpoint.

The freezing of the coal in wet washing when the drying has been done as described above, is not of very much importance, because coal with 5 per cent, or even 6 per cent moisture, will not freeze as long as it has no free water in it. We have already told you that dewatering bins, centrifugal driers, etc., are on the market and in general use in an up-to-date wet washing plant. Consequently, the advantages of transportation claimed by the dry crowd as one of the special advantages of dry cleaning in having the possibility of shipping dry coal, is true as long as the run-of-mine coal is dry, but if the run-of-mine coal becomes wet, this advantage is not so apparent and not

only that, but the dry washing plant will be of no efficient use if the coal is wet.

It is also extremely doubtful if the dry coal carried during rainy days will not absorb moisture which would be divided in a very irregular way. This also reduces the advantages of dry cleaning for fine coal.

We also doubt if the customer prefers unloading dry and dusty coal rather than damp coal, for the handling of dry and dusty coal presents some dust nuisances at many unloading points where water sprays are used to allay the dust.

### IS THERE A BEST WASHING SYSTEM?

We had in mind to compare the two processes, jigs and Rheolaveur, used almost exclusively in Europe. After thinking it over, it seems to us that this comparison was less interesting than the question of knowing which one may have, or if it has, a better process of coal washing. As a general and an immediate answer, it can be said, without doubt, that all the various processes can be advantageously used for special cases, and, then reasonably is it not a better process of washing that can handle all cases, rather than having a special washer for each particular case? Such questions seem full of good sense, and furthermore, is it not true?

As we know, the purpose of the washing operation is to make always the separation by gravity, and so we will have to grant that the best process is the one that can make this separation in the most perfect way, when this process by its arrangement allows the application of all the principles on which it is based in such a way that it is possible to solve all the washing problems. Sometimes it is apparent that a washing process can permit several combinations, or arrangements, each suitable for some particular case, with of course, the conditions that such arrangement does not bring in too many complications and expense which would prohibit them. In this respect we feel that the Rheolaveur process has shown itself adaptable to all washing problems, no matter if the raw coal is clean or very dirty, if it is easy or difficult to wash on account of the large amount of particles of intermediate gravity, if it contains dust or not, if it is wet or has flat slate, if it is composed of particles having a high or low gravity, no matter if it is anthracite or bituminous, or if it is necessary to meet the most difficult market conditions. With the Rheolaveur process, the proper separation solves directly all the

problems in a successful way. It can also solve very well the known difficulties of washing the sludge by making from this dust an excellent and valuable product. It allows the washing of coal from 0 to 5 inch, reducing therefore, the cost of hand-picking on the tippie, as everyone acquainted with the cleaning of coal, realizes that  $2\frac{1}{2}$  inches by 5 inches coal is very difficult to clean efficiently by hand and is very expensive work. If it is required, the Rheolaveur process can at any time separate in order to make a class of boiler fuel or middling product which it is sometimes necessary to do in order to have washed coal with a low ash content. If there is no use for such middlings, they can always be crushed and rewashed with the feed coal, thus always rendering the best condition for obtaining efficiency.

In any case the initial cost of a Rheolaveur washing plant will always be low as compared with other types giving the same efficient washing; the same applies to the operating cost. A washing plant ought always to be built to solve all the washing problems, no matter what they are. In most of the coal mines, the seam of coal often completely different in structure and comparison, is worked simultaneously or successively. The market conditions at one time may require extremely clean coal and at another time, the washed coal can be of any quality, but in all cases, the refuse has to be as perfect as possible. In a new coal mine the coal may come out dry in the beginning, but after several years, it may become a wet mine. If the coal has to be hauled from the mine to the cleaning plant several miles, it may get wet. The Rheolaveur process has thus far passed successfully through all the difficulties. I ask you, is there any other process which can be compared with it, taking into account all the operating conditions above mentioned? We do not think that there is *one* and the reason is because the Rheolaveur process makes the separation by natural gravity, where the other processes made the separation, more or less, by equivalence, which requires a presizing of the coal if it is necessary to wash with appreciable efficiency, and it is well known how difficult it is to make an efficient screening, especially on the small sizes, which is the first weak point in nearly all the other processes.

On the other hand, the separation by fluids—either air or water—the case of Rheolaveur process excepted—is always characterized by the use of an upward current which is opposed to the deposit of finest particles and this action has the tendency to float the flat slate and it is entirely inefficient for the stratification of the

middlings. While it would be advantageous to have a bed of refuse as compact as possible in order to avoid the introduction of coal into the voids between the big pieces, it is absolutely necessary to allow the action of the classifying medium to loosen up this mass of slate and middlings, and, by so doing, the coal is given ample opportunity to pass among the refuse.

In the wet process the dust disturbs the efficiency and in the dry process the dust is not cleaned at all. This increases the sulphur, which is inimical for coking coal. Furthermore, moisture is a disturbing factor in dry cleaning processes. Each of all processes, with the exception of the Rheolaveur, is available for application with satisfactory results in very special cases in order to meet special conditions, but if the condition has to be changed, then the process will be no longer satisfactory, at least as far as the economics of washing is concerned.

We have made this comparison by placing ourselves in an objecting position, wishing to attract discussions, and although on the other side of the fence, we wish to make it known that we have been immensely interested in the progress of the American people in coal cleaning, especially, the dry cleaning processes and in the facts evident to all of us as to what can happen with an intelligent will-power and tenacity in an idea, which, a few years ago was considered as an Utopia, even by eminent specialists in the matter, and then one finds among the business men, support and co-operation which are the accepted and current practices among the people of this great country.

## INTERPRETATION OF FLOAT-AND-SINK DATA<sup>1</sup>

By B. M. BIRD

*Supervising Engineer, U. S. Bureau of Mines, Southern Experiment Station, Tuscaloosa, Alabama*

Every one concerned with the cleaning of coal is frequently faced with the problem of interpreting the results of washability tests, such as float-and-sink tests, screen-sizing tests, and other operations supplementary to them. One coal operator may be planning to clean a coal that heretofore has only been screen-sized and hand-sorted. He has before him a complete series of float-and-sink data on a number of sizes of his coal, and on a number of other coals, together with results obtained in washing those coals by various processes. (The term "washing" is used loosely in this paper to include dry as well as wet methods.) From these data the operator wishes to estimate what yields from his coal of the kind of coal he desires can reasonably be expected from each washing process. Another coal operator who is already washing his coal wishes to compare the performance of his plant with that of other plants. The first step of both men, whose problems are essentially the same, must be a comparison of the problem of washing their coals with that of washing the coal treated at any given plant. Either man may find that his coal differs from the other coal in one or more of the following particulars: His raw coal may contain 15 per cent ash and the other 25 per cent ash. His coal may have a proportion of low-ash coal, say under 2 per cent ash, three times as large in amount as found in the other coal. Again, it may contain only one-half as much material between 1.40 and 1.70 specific gravity which is the range of specific gravity of material that in bituminous coals is usually designated as bone coal or bone. For these reasons the other coal is harder to wash to some given ash content than his own. On the other hand, his fine slack through  $\frac{3}{16}$ -inch may be 5 per cent higher in ash content than the equivalent size of the other coal, and further, it may contain a shale that disintegrates more readily in water than that found with the other coal. In these last particulars his problem is the more

<sup>1</sup> Presented by permission of the Director, U. S. Bureau of Mines, before the Second International Conference on Bituminous Coal, Pittsburgh, Pa., November 19 to 24, 1928. (Not subject to copyright.)

difficult. Moreover, when he examines the results obtained in washing the other coal he may find that it has been washed only to 10 per cent ash, whereas he must wash his coal to 7 per cent ash. How can either operator use these data and make a fair approximation as to what results he should expect from his coal if it could be substituted for the other coal and washed with equal skill to the ash content he requires?

The answer to this question must of necessity depend upon some method of comparing the relative difficulties of the washing problems. If the operator could be sure by some means that the problem of washing the other coal to 10 per cent ash was equal to or more difficult than that of washing his coal to 7 per cent ash, he would be safe in expecting at least equal efficiency by treating his coal in that plant. That is, if that plant in preparing a washed coal containing 10 per cent ash recovers 90 per cent of the yield shown by float-and-sink tests, he may reasonably expect 90 per cent of his float-and-sink yield at 7 per cent ash. Now a determination of whether two washing problems are equally difficult depends, first, on some comparison of their float-and-sink data; and second, on some fair evaluation of other factors, such as variations in the screen-analyses, in the proportions of flat-shaped particles, and in other particulars. It is primarily with the problem of putting float-and-sink data on a comparative basis that this paper is concerned. A comparative basis in turn makes it possible to translate them by use of existing data on the washing of other coals, into terms of actual washing, this being the essential thing desired in the interpretation of float-and-sink data. However, as float-and-sink data by no means tell the whole story in the comparison of two coals, other factors affecting the problem will be touched upon briefly.

#### SOME PREVIOUS METHODS OF INTERPRETING FLOAT-AND-SINK DATA

A number of different methods have been advocated for interpreting float-and-sink data, of which only a few will be mentioned. In the simplest method the investigator compares the difficulties of removing the impurities from two coals entirely by the proportions of the different specific gravity fractions obtained with the heavy liquids. On the basis of the proportions of bone and shale present, he compares the difficulties of the specific-gravity separa-

tions for different coals. This method in graphical form<sup>2</sup> is shown in Figure 1, which has been prepared by calculating a number of the data of Table I to show how they would appear if the same specific gravities of solutions had been used throughout. However, the methods in commonest use are based upon the shape of certain of the washability curves. As the method proposed herein also involves the use of one of those curves, each of them will be discussed briefly.

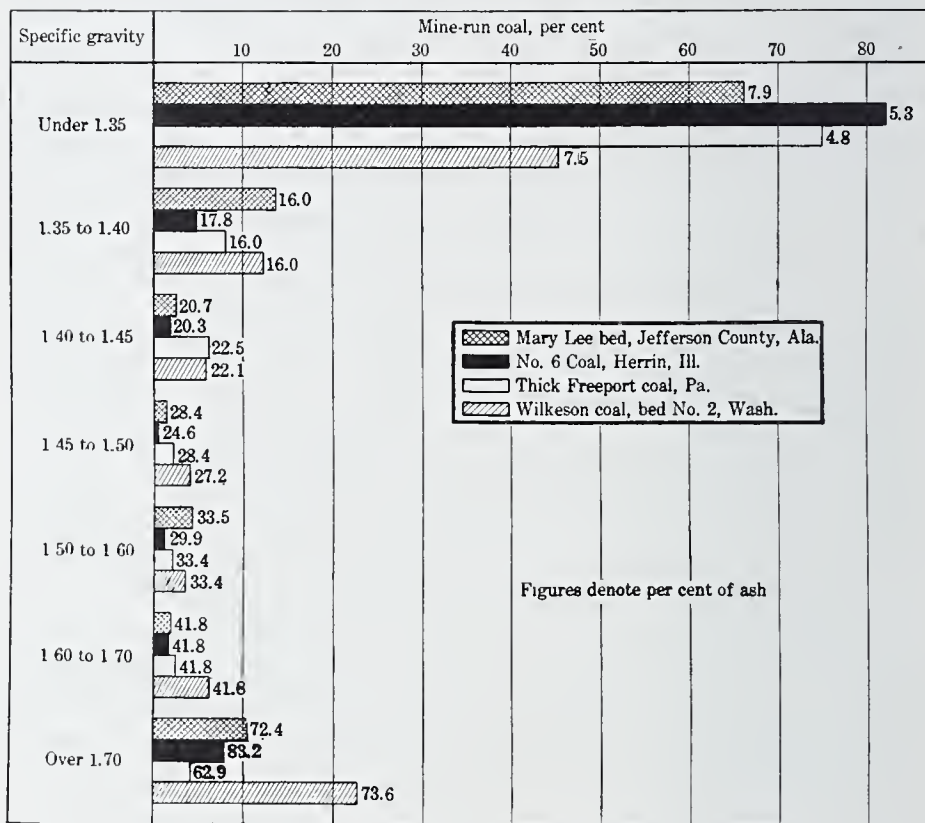


FIG. 1. CHART SHOWING RELATIVE PROPORTIONS OF SPECIFIC GRAVITY FRACTIONS IN TYPE COALS

(After Fraser and Yancey)

### *Use of the Cumulative Curve*

Plotting the curve of cumulative weight per cent against cumulative ash per cent has been advocated by some investigators as a

<sup>2</sup> Fraser, Thomas, and Yancey, H. F., Cleaning Tests of Central Illinois Coal. Tech. Paper 361, Bureau of Mines, 1925, p. 10.

means of determining the difficulty of washing problems. It is so widely used that little need be said of its construction. The necessary calculations of the data to give the cumulative weight per cent

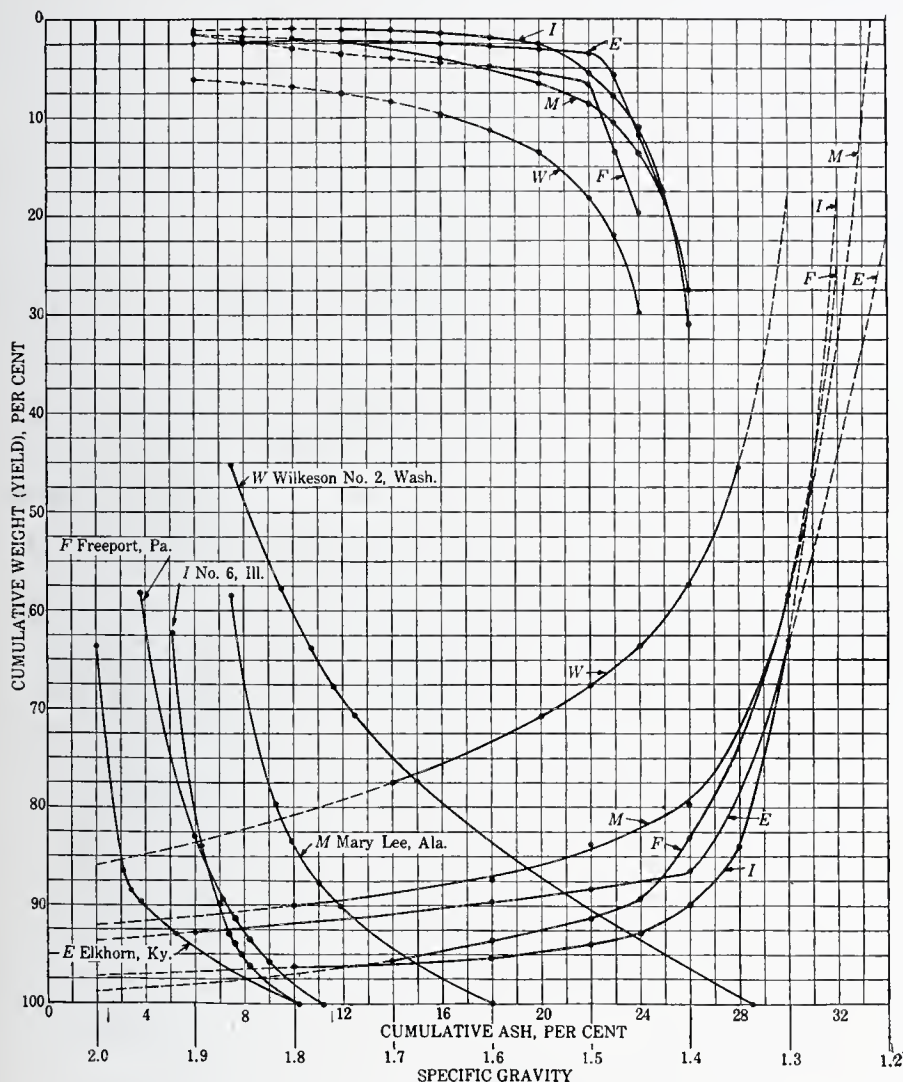


FIG. 2. TYPE COALS—CURVES OF CUMULATIVE WEIGHT PER CENT AGAINST CUMULATIVE ASH PER CENT (LEFT), AGAINST SPECIFIC GRAVITY (RIGHT), AND AGAINST  $\pm 0.10$  SPECIFIC GRAVITY DISTRIBUTION (TOP)

and cumulative ash per cent are shown in full in Table I in the two columns at the right. These cumulative data are plotted at the left of Figure 2. (The specific gravity curves at the right and the specific

TABLE I

FLOAT-AND-SINK DATA OF TYPE COALS FROM VARIOUS PARTS OF THE UNITED STATES

	SPECIFIC GRAVITY	WEIGHT	ASH*	CUMULATIVE WEIGHT	CUMULATIVE ASH*
		<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
No. 6, Illinois†.....	Under 1.30	62.4	5.1	62.4	5.1
	1.30-1.35	21.6	9.8	84.0	6.3
	1.35-1.40	5.9	16.1	89.9	7.0
	1.40-1.45	3.0	20.9	92.9	7.4
	1.45-1.50	1.1	26.0	94.0	7.6
	1.50-1.60	1.2	31.2	95.2	7.9
	1.60-1.80	1.0	37.7	96.2	8.2
	Over 1.80	3.8	60.4	100.0	10.2
Mary Lee, Ala.‡.....	Under 1.30	58.6	7.5	58.6	7.5
	1.30-1.40	21.2	14.3	79.8	9.3
	1.40-1.50	3.8	23.4	83.6	9.9
	1.50-1.60	4.1	33.5	87.7	11.0
	1.60-1.80	2.3	43.9	90.0	11.9
	Over 1.80	10.0	73.4	100.0	18.0
Elkhorn, Ky.§.....	Under 1.30	63.7	2.0	63.7	2.0
	1.30-1.40	22.7	6.1	86.4	3.1
	1.40-1.50	1.9	19.3	88.3	3.4
	1.50-1.60	1.3	28.0	89.6	3.8
	1.60-1.90	3.3	43.4	92.9	5.2
	Over 1.90	7.1	76.4	100.0	10.2
Freeport, Pa.**.....	Under 1.30	58.2	3.8	58.2	3.8
	1.30-1.40	24.8	10.9	83.0	5.9
	1.40-1.45	6.3	22.5	89.3	7.1
	1.45-1.50	2.1	28.4	91.4	7.6
	1.50-1.60	2.1	33.4	93.5	8.2
	1.60-1.70	2.4	41.0	95.9	9.0
	Over 1.70	4.1	62.9	100.0	11.2
Wilkeson No. 2, Wash.††.....	Under 1.35	45.4	7.5	45.4	7.5
	1.35-1.40	12.3	16.8	57.7	9.5
	1.40-1.45	6.0	22.1	63.7	10.7
	1.45-1.50	4.0	27.2	67.7	11.6
	1.50-1.55	3.1	32.0	70.8	12.5
	1.55-1.70	6.5	42.2	77.3	15.0
	Over 1.70	22.7	73.6	100.0	28.3

gravity distribution curves at the top will be explained later.) These curves show the average ash content of all of the coal included at any selected yield. They serve as a basis for the computation of the efficiency of washing, which is 100 times the yield per cent by washing divided by the yield shown by the cumulative float-and-sink curve for the same ash content.

Several ways have been suggested for deducing from these curves the comparative difficulty of the specific gravity separation. One makes use of the sharpness of the bend in this curve where it tends to flatten out at high percentage yields. A sharp bend indicates a marked rise in the ash content of the materials included at that point and hence a marked increase in their specific gravity. If made at an ash content, well beyond a sharp bend in the cumulative curve, the separation according to this method is classed as comparatively easy. Another method is to draw a tangent to the curve at the point indicating the ash content desired in the washed coal, and from the steepness of the slope to estimate the difficulty of the separation according to specific gravity.

Though all of these schemes in the hands of the skilled and experienced engineer yield some information, most men have found the elementary curve more satisfactory because it shows in accentuated form the increase in ash content, and therefore in specific gravity, at high yield percentages.

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\* Moisture-free basis.

† Illinois, No. 6 bed, Franklin County, 3-inch by 6-inch egg crushed to pass a  $\frac{3}{4}$ -inch round-hole screen.

‡ Alabama, Mary Lee bed, Jefferson County, run-of-mine crushed to pass 1-inch round-hole screen.

Yancey, H. F. and Fraser T.; Coal Washing Investigations: Bull. 300 Bureau of Mines, 1928 (In preparation).

§ Kentucky, Elkhorn bed, Letcher County (Campbell says "Modified from Elkhorn seam"), 4-inch to  $\frac{5}{16}$ -inch.

Campbell J. R., Cleaning Bituminous Coal: Tech. Pub. 117, Am. Inst. Min. and Met. Engs, New York meeting, February, 1928, p. 9.

\*\* Pennsylvania Thick Freeport bed, Allegheny County, run-of-mine crushed to pass about  $1\frac{1}{4}$ -inch round-hole (15 per cent on 1-inch round).

Yancey, H. F., Washing Characteristics of Coal From the Thick Freeport bed, Pennsylvania: Bull. 16, Coal Mining Investigations, Carnegie Inst. of Tech., 1924, p. 18.

†† Washington, Wilkeson No. 2 bed, Pierce County, run-of-mine coal passing a 3-inch round-hole screen.

McMillan, E. R., and Bird, B. M., Coal-Washing Problems of the Pacific Northwest: Bull. 28, University of Washington Experiment Station, 1924, p. 165.

*Use of Elementary Curve*

Just as the curve of cumulative weight per cent against cumulative ash per cent gives the average ash content of all of the material included at any given yield, so the curve of elementary ash per cent for this same yield per cent gives the ash content of the last infinitely small product included in that average. This curve can be plotted directly from the float-and-sink data if a great number of solutions are used. However, because of the amount of routine labor involved in that method, it is more satisfactory to use only a few solutions, and to work back to the elementary curve from the cumulative

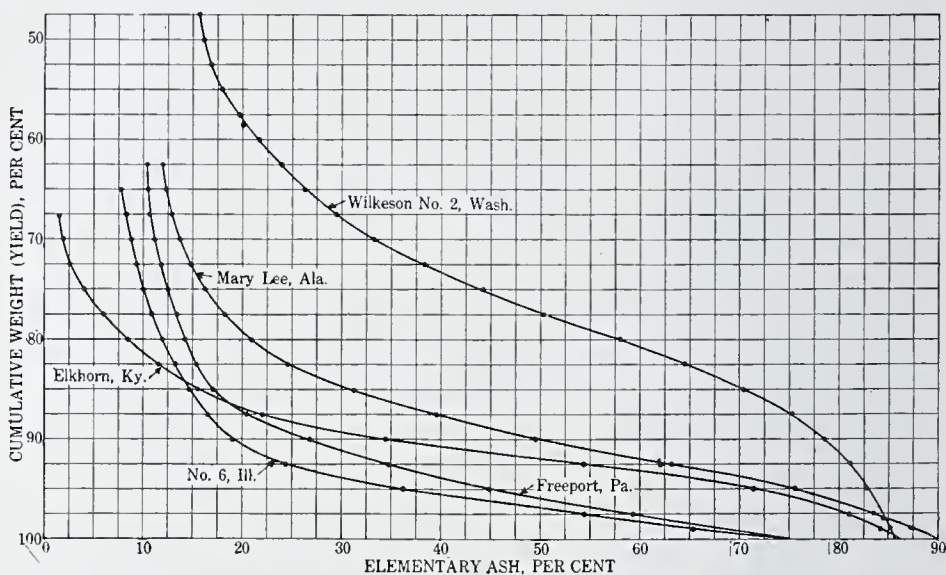


FIG. 3. TYPE COALS—ELEMENTARY CURVES

curve. The method used for constructing the different elementary curves in Figure 3 is illustrated in Table II. Each weight percentage is multiplied by its ash percentage and the resulting units of ash are cumulated to give cumulative units of ash. A curve of cumulative units of ash against cumulative weight per cent is then constructed on a large scale by use of a set of splines and weights. Suppose that the elementary ash percentage is desired at a yield of 90 per cent: Then the cumulative units of ash at 87.5 per cent are subtracted from those at 92.5 per cent and the difference is divided by 5 ( $92.5 - 87.5$ ). The quotient is the desired elementary ash percentage at a yield of 90 per cent.

Because of the mathematical relationship between the elementary curve and the cumulative curve, the same methods are used for interpreting them. In the elementary curve, however, the slope of a tangent to the curve near the specific gravity at which the separation is to be made is a much more reliable guide to the comparative difficulty of the washing problem than is the same tangent on the cumulative curve because this curve shows directly the change of ash content with increasing yield.

### *Use of Specific Gravity Curve*

The curves of specific gravity against cumulative weight per cent at the right of Figure 2 show directly the variation of specific gravity with increasing yield. The specific gravity curve is usually inter-

TABLE II  
CALCULATIONS FOR ELEMENTARY ASH CURVE, ELKHORN COAL

WEIGHT		ASH		UNITS OF ASH	CUMULATIVE UNITS OF ASH	CUMULATIVE WEIGHT
<i>per cent</i>		<i>per cent</i>				<i>per cent</i>
63.7	×	2.0	=	127.4	127.4	63.7
22.7	×	6.1	=	138.5	265.9	86.4
1.9	×	19.3	=	36.7	302.6	88.3
1.3	×	28.0	=	36.4	339.0	89.6
3.3	×	43.4	=	143.2	482.2	92.9
7.1	×	76.4	=	542.4	1,024.6	100.0

preted by means of tangents in much the same manner as the cumulative and the elementary curves and is generally studied in combination with the other curves. However, it seems that its possibilities have not been fully explored by many engineers. As will presently appear, the specific gravity curve is the curve upon which the method of interpretation herein described is based.

## PROPOSED METHOD OF INTERPRETATION

### *Principles Involved*

The relative specific gravities of the particles of coal and impurities, if shape and size of particle be temporarily eliminated from consideration, is an indication of the difficulty of their separation. This is self evident for processes dependent upon specific gravity. It

is almost equally so for other processes. Any process that removes ash forming impurities from coal depends upon some physical or chemical property that varies according to the ash content of the coal. As the specific gravity of coal varies almost directly with ash content, these other physical properties must also vary with specific gravity. This is simply a modification of the old axiom that things equal to the same things are equal to each other. Therefore, any evaluation of the difficulties of a washing problem for all processes may be based directly or indirectly upon relative specific gravities. However, "coal" is not a mineral substance of definite specific gravity, and neither are the impurities associated with it in mining. The components of every raw coal range in specific gravity by small differences, from that of the very cleanest coal to that of shale. It is on this account that for the purposes of coal washing it is necessary to establish for each mine some arbitrary standard, either one of ash content or of specific gravity, defining what is coal and what is impurity. For example, a standard may be set that all particles of less than 1.50 specific gravity are coal and all particles of more than 1.50 specific gravity are refuse. But, even after this standard has been set, relative specific gravity taken by itself has no special significance in comparing the washing problems of two different coals. In a separation at 1.50 specific gravity the relative specific gravities range over comparatively wide limits. For a particle of 1.501 and one of 1.499, the relative specific gravity is  $\frac{1.501}{1.499}$ , or just a trifle more than unity. For a particle of coal of 1.25 specific gravity and one of shale of 2.50 specific gravity the relative specific gravity equals  $\frac{2.50}{1.25}$ , or 2.0. Since this is the condition in all coals, evidently some other factor must be taken into consideration besides relative specific gravity in comparing the difficulties of washing them.

The other factor to be considered is the proportions of the different specific gravity units to be separated. For example: suppose that a raw coal could be found, three-fourths of which was composed of particles between 1.45 and 1.55 specific gravities. Obviously a very sharp separation at 1.50 specific gravity would be much more difficult to obtain with such a coal than in a coal of which three-fourths was less than 1.30 and more than 1.70 specific gravities. From this illustration it will be evident that a method of measuring the comparative difficulty of a separation according to specific gravity must

take into account the distribution of all of the specific gravity components of the raw coal with respect to the point of separation. Curves showing such a distribution for a separation at 1.50 specific gravity, with a correction to be explained presently, are shown in Figure 4. As an illustration of the method of reading the curves take Wilkeson No. 2 coal from Washington. It contains 8.3 per cent

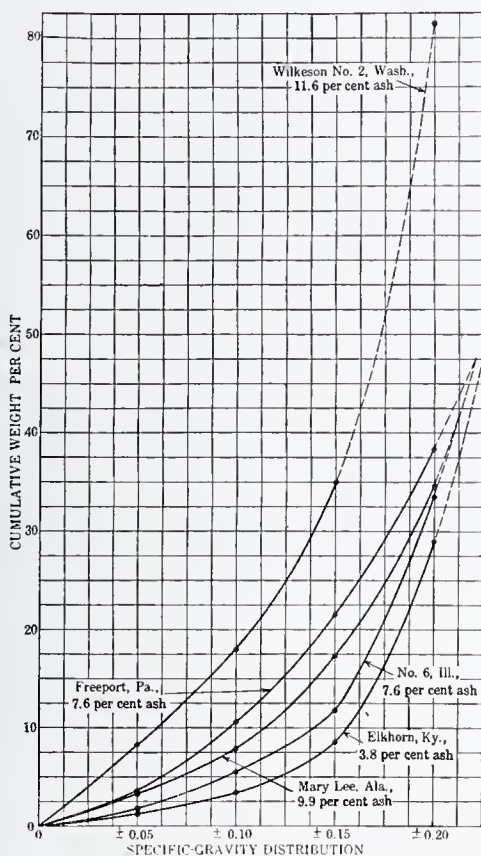


FIG. 4. TYPE COALS—SPECIFIC GRAVITY DISTRIBUTION CURVES FOR 1.50 SPECIFIC GRAVITY

in the range  $\pm 0.05$  specific gravity—that is, between 1.45 and 1.55; 18 per cent in the range  $\pm 0.10$  specific gravity, that is, between 1.40 and 1.60; 35 per cent in the range  $\pm 0.15$  specific gravity, that is, between 1.35 and 1.65, etc.

The rapidity of the rise of these curves indicates the difficulty of separation according to specific gravity. For instance: the Elkhorn curve shows a very gradual rise and the Wilkeson a compara-

tively rapid rise. If the curves coincide for two coals at some specific gravities not necessarily the same, evidently the separations so far as specific gravity is concerned are equally difficult. If other factors such as shape and size of particle be disregarded for the moment, it is a fair assumption that equally good efficiencies should be attainable for both coals with the same washery and the same skill of operation. Thus if a new coal must be washed at some specific gravity, say at 1.45, to produce a coal of some required ash content, a specific gravity distribution curve can be constructed and compared with the curves of other coals perhaps being washed at entirely different specific gravities. When the specific gravity distribution curve of the coal on which the washing results are known coincides with or rises on the average equally or more rapidly than that of the new coal, the results, so far as specific gravity is concerned, may be safely applied to the prediction of what results should be obtained from the new coal.

At this point a natural question intrudes itself as to whether the apparent specific gravity of the medium of coal and water in the washers on which the results are to be used should be considered in making a comparison between the two problems of washing the coals. For example, a recent measurement at approximately the dividing line between washed coal and refuse in a jig showed an apparent specific gravity of over 1.5. As this jig was making a separation at about 1.7, the actual relative specific gravities of particles of 1.6 and of 1.8 in the jig bed were about as follows  $\frac{1.8 - 1.5}{1.6 - 1.5} = \frac{0.3}{0.1} = 3$ .

In this manner the coal-water mixture greatly increased the relative specific gravities of the coal and impurities over those in air. The question is: Should any factor of this kind be considered? A moment's thought indicates that it should not be considered, at least for bituminous coal. The apparent specific gravity of the medium is an inherent property of any given process and the result of it is reflected in the capacity of the washers to handle a large range of sizes in one operation. Furthermore, the density of the coal-water mixture varies for every washer even of the same kind, depending upon the adjustment. As only average figures could be used, this factor would be uncertain. Again, such a correction would only alter the proportions of the picture shown in Figure 4 and not any conclusion reached by its use. Accordingly, it is believed that this factor need not be considered for bituminous coals, and that specific

gravity distribution curves such as these, based upon specific gravities in air, may be made the basis for comparing the difficulties of cleaning two coals of that rank. However, if results of washing bituminous coals are to be applied to anthracite coals of higher specific gravity, a correction may be necessary, but what it should be can not be stated at this time.

A second principle involved in the use of the specific gravity distribution curve is that the difficulty of a washing problem varies

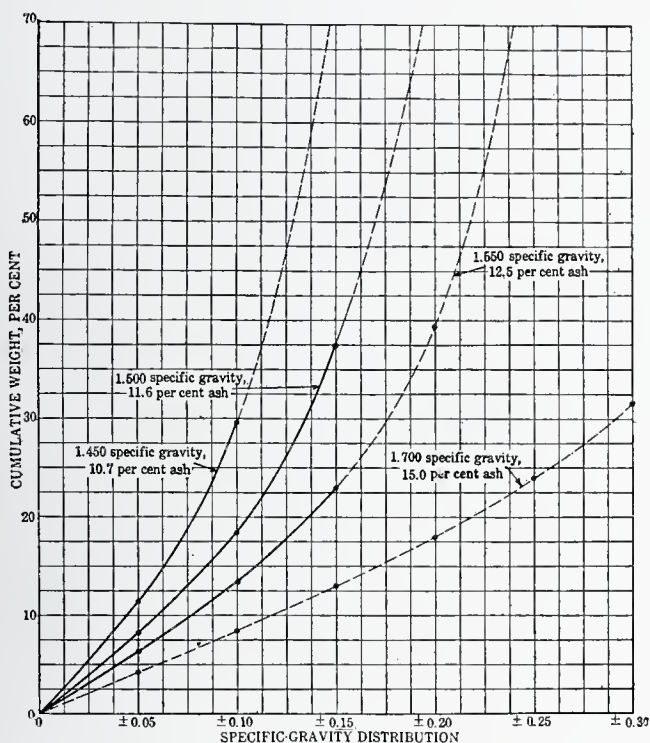


FIG. 5. SPECIFIC GRAVITY DISTRIBUTION CURVES FOR WILKESON WASH., COAL, SHOWING INCREASING DIFFICULTY OF WASHING TO LOW ASH CONTENT

according to the ash content or specific gravity at which the coal must be washed. As this principle is fundamental to any method of applying washing results from one coal to another, it has been demonstrated in Figures 5 and 6, showing specific gravity distribution curves at several specific gravities for two coals differing markedly in washing characteristics. The sharp rise of these curves in both coals for a separation at 1.45 indicates clearly that either of them becomes extremely hard to wash if washed coals of low enough ash

content must be produced. They indicate clearly the fallacy of assuming that because a process is efficient in a separation at 1.70 specific gravity it is necessarily efficient at 1.45 specific gravity. Because of the increased difficulty of the separation at the lower specific gravity the process may be hopelessly inefficient. Note the rapid increase in the proportions of the Illinois No. 6 coal within  $\pm 0.15$  specific gravity: 1.7 per cent at 1.70; 6.1 per cent at 1.55; 11.6 per cent at 1.50; and 33.5 per cent at 1.45. This last proportion at 1.45

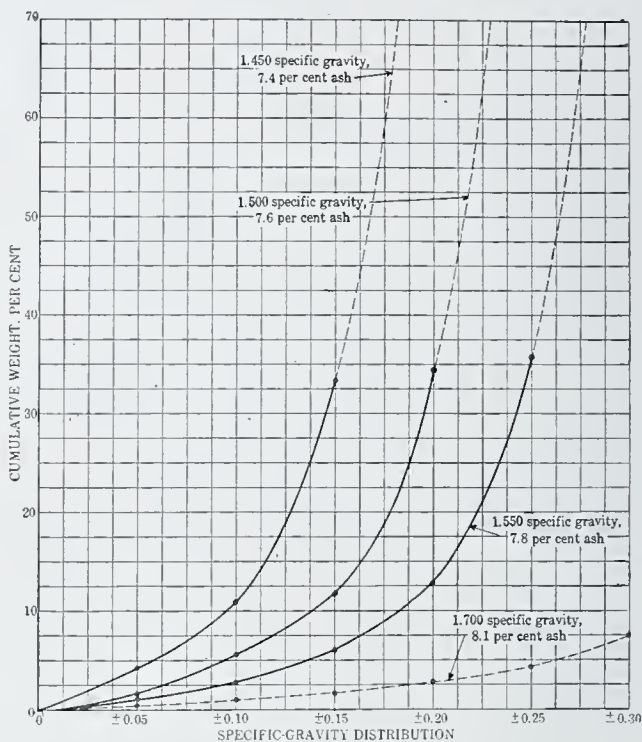


FIG. 6. SPECIFIC GRAVITY DISTRIBUTION CURVES FOR No. 6, ILLINOIS, SHOWING INCREASING DIFFICULTY OF WASHING TO LOW ASH CONTENT

specific gravity indicates how very difficult a separation may become if the requirements as to ash content are severe enough. The Wilkeson coal from Washington shows these same characteristics, but of course the curves for the same specific gravity are quite different. However, it is not hard to see that two specific gravities exist in the two coals at which the separations are equally difficult.

A third principle involved in the use of the specific gravity distribution curve is concerned with a correction thus far ignored. All

float-and-sink data to be on a comparative basis must be corrected to a common percentage of material of high specific gravity. If that is not done an anomalous situation could exist where the addition of 10 per cent of roof rock, though greatly raising the ash content of the raw coal and lowering the percentage of recoverable washed coal, would apparently make a given coal easier to wash because it would decrease the percentages near the point of separation; this would be absurd. The addition of roof rock to a coal, if anything, would make the separation at the same specific gravity more difficult. In the comparison of several coals the presence of varying proportions of roof rock obscures the real washing problem. The difficulty of a washing problem depends largely upon the percentages of materials with  $\pm 0.20$  specific gravity of the point of separation. On this account, materials of very high specific gravity must be brought to a common basis. Strictly speaking, not only should this be done but also some factor should be applied to the percentages remaining to take care of the greater difficulty occasioned by the presence of more of this material in one coal than in another. Suppose for example, that 10 per cent of material of over 2.00 specific gravity is found in one coal and 20 per cent in another. These coals might be put on a common basis as to impurities of high specific gravity by multiplying each percentage to be used in the specific gravity distribution curves by  $\frac{100}{90}$  for the first coal and  $\frac{100}{80}$  for the second coal; this step would eliminate from consideration all material of over 2.00 specific gravity. However, if the two coals were identical in washing characteristics in every other particular, the second coal would be slightly more difficult to wash. But as the amount of the additional correction necessary is uncertain, the specific gravity distribution curves and all curves derived from them have thus far been corrected only to eliminate material above 2.00 specific gravity. The specific gravity of 2.00 has been chosen because it is as high as existing specific gravity curves can be extrapolated with any degree of accuracy.

### *Construction of Curves*

After the preceding explanation of the correction to be applied to specific gravity distribution curves, their construction is a mere matter of detail. The uncorrected data for the specific gravity distribution curve are obtained directly from specific gravity curves

such as shown to the right at the bottom of Figure 2. Suppose one of the specific gravity distribution curves, say that for the Mary Lee coal, is to be constructed for a separation at 1.50 specific gravity. The yield percentages for  $\pm 0.05$  specific gravity—that is, between 1.45 and 1.55—are read from the specific gravity curve, and the difference is determined. Similarly, the yields for  $\pm 0.10$  specific gravity are determined by subtracting the yield for 1.40 from that at 1.60. This procedure is continued by intervals of 0.05 specific gravity or less until enough points are obtained for the construction of the distribution curve. The percentages so determined are corrected to eliminate all material above 2.00 specific gravity by multiplying them by 100 and dividing by the percentage under 2.00 specific gravity. Corrected percentages have been used on all specific gravity distribution curves or curves based upon them.

Generally float-and-sink data are not carried to very high or to very low specific gravities and the specific gravity curve has to be extrapolated. Whenever extrapolation has been resorted to in this paper the curve has been shown in dotted lines. These extrapolations have not been made haphazardly. The high specific gravities have been plotted by placing a No. 48 ship curve so that the curved portion coincides with the bottom of the known portion of the curve and the other end crosses 100 per cent at 2.65 specific gravity. For low specific gravities the ash content of the coal under 1.30 or under 1.35, as the case happened to be, was used as a guide to indicate how much of the coal was under 1.25 specific gravity.

Specific gravity distribution curves constructed in this manner show the true difficulty of a separation according to specific gravity. They are the basis of the method used in this paper. If this is kept in mind the various details of applying this scheme to the solution of washing problems will be followed easily.

## APPLICATION TO PRACTICAL PROBLEMS

### *Determination of Points of Equal Difficulty*

One problem in the use of the specific gravity distribution curves has been to devise a short-cut method of determining approximately when the separations according to specific gravity are equally difficult. A possible method has been suggested by the percentages of materials within  $\pm 0.10$  specific gravity shown in Figures 4, 5, and 6; the part of a curve covering that range of specific gravities seems to

afford an index to the general character of the entire curve. In order to study the result of using just that much of the curves, the  $\pm 0.10$  specific gravity curves at the top of Figure 2 were constructed. These curves show at any specific gravity the corrected percentage of each coal within  $\pm 0.10$  specific gravity for each specific gravity. For example, at 1.40 specific gravity the curve at the top shows the

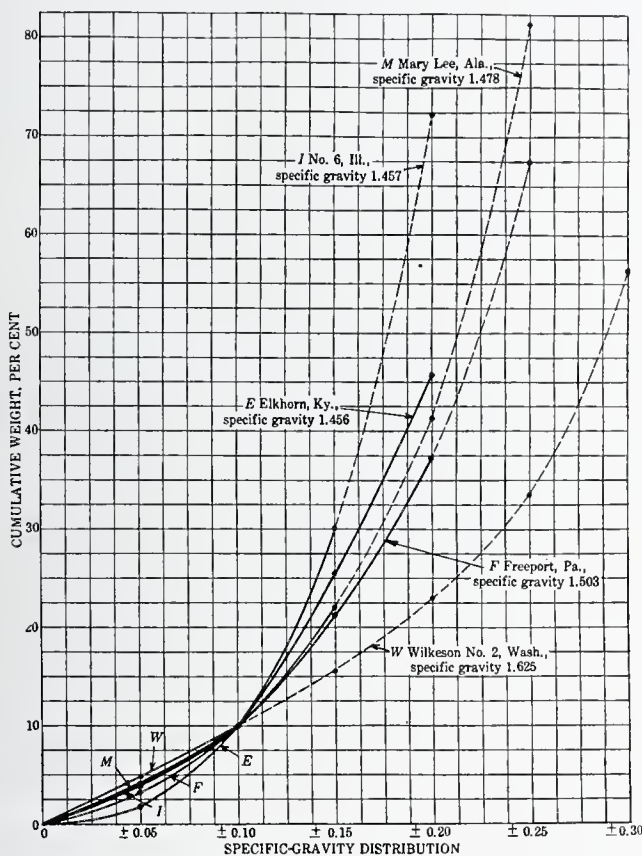


FIG. 7. TYPE COALS—COMPLETE SPECIFIC GRAVITY DISTRIBUTION CURVES FOR POINTS HAVING 10 PER CENT WITHIN  $\pm 0.10$  SPECIFIC GRAVITY

percentage between 1.30 and 1.50, corrected to eliminate all material above 2.00 in specific gravity. These curves were used to find points where 10 per cent of each coal was within  $\pm 0.10$  specific gravity, and the complete curves in Figure 7 were constructed. Since the points so located were certainly at least approximately correct, these curves demonstrated that it was not possible to find points of equal difficulty at which the curves for all the coals coin-

cided; this outcome is to be expected from the shapes of the specific gravity curves from which the complete specific gravity distribution curves are constructed.

The curves cannot coincide, and yet points undoubtedly exist where the specific gravity separations are equally difficult. A second problem therefore becomes apparent, that of finding some means of telling when two curves represent equally difficult problems. Evidently the scheme used must involve averaging the conditions between 0 and  $\pm 0.10$  specific gravity against those beyond  $\pm 0.10$  specific gravity. For instance, in Figure 8 the Washington coal

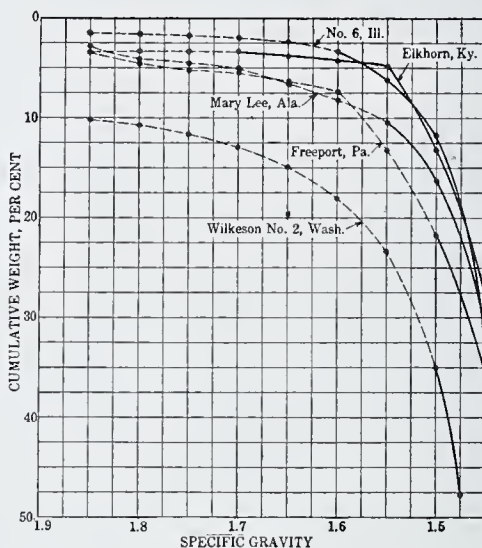


FIG. 8. TYPE COALS— $\pm 0.15$  SPECIFIC GRAVITY DISTRIBUTION CURVES (TO BE USED WITH CUMULATIVE AND SPECIFIC GRAVITY CURVES IN FIGURE 2)

risers more rapidly than the Illinois coal up to the  $\pm 0.10$  point, and therefore is more difficult to wash so far as that range is concerned. But the Illinois curve rises more rapidly above the  $\pm 0.10$  specific gravity point; therefore so far as that range is concerned, the Illinois coal is more difficult to wash. Some balance must be struck between these two conditions. Since the difficulty of a problem of coal washing depends mainly upon the percentages within  $\pm 0.20$  or  $\pm 0.25$ , any method that will average conditions in that range will be satisfactory.

A satisfactory balance has obviously not been obtained in Figure 8; the spread of the curves beyond the point where they cross is

much greater than it is between that point and the origin of the curves. As a better balance apparently would result if larger percentages of the total coal were involved, a set of curves was plotted by use of Figure 8 and Figure 2 to show the result of using an interval of  $\pm 0.15$  specific gravity and of choosing a point where 15 per cent of the coal is involved; these curves would cover roughly the same points of difficulty as are shown by the curves in Figure 8. The resultant balance in Figure 9 appears to be satisfactory. (Incidentally, these curves suggest that equal areas under the curves up

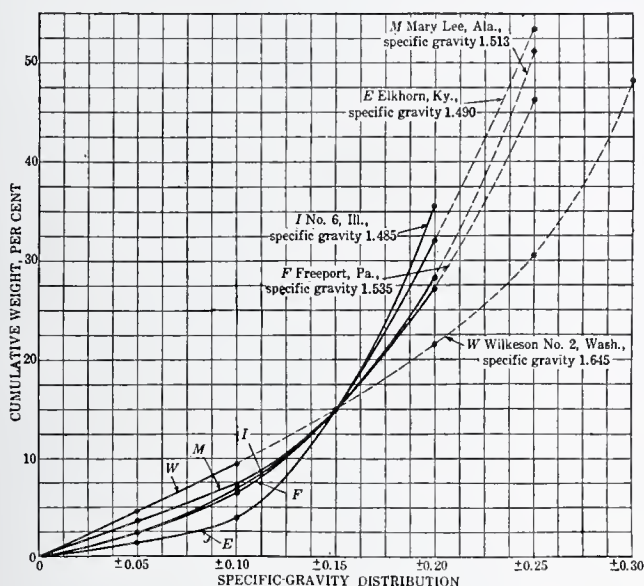


FIG. 9. TYPE COALS—COMPLETE SPECIFIC GRAVITY DISTRIBUTION CURVES FOR POINTS HAVING 15 PER CENT WITHIN  $\pm 0.15$  SPECIFIC GRAVITY

to  $\pm 0.20$  might be used to judge when the optimum point for the curves to cross has been found.)

The method of obtaining a good balance of the curves is to provide larger intervals above and below the point of separation; this step in turn involves a larger percentage of the coal. If a large percentage of the coal is involved by an interval  $\pm 0.10$  specific gravity, that material gives a very well balanced set of curves. A comparison of Figures 9A and 7 shows this well. Figure 9A shows the same separation as Figure 7 except that the separation involves 20 per cent of the different coals on a corrected basis in place of 10 per cent. This curve shows a very good average condition and the specific gravities

for equal points of difficulty so determined can be taken as being correct enough for all practical purposes.

The fact that the  $\pm 0.10$  specific gravity distribution curve serves admirably for determining points of equal difficulty where the separation is difficult—that is, where large percentages are involved—suggests that it might be sufficiently accurate to be used over the entire range of specific gravities. It is true that as the percentages of coal involved decrease, the condition obtains that is depicted in

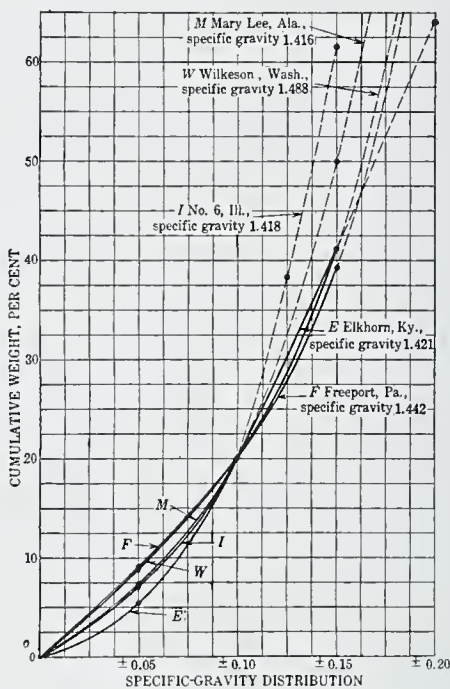


FIG. 9A. TYPE COALS—COMPLETE SPECIFIC GRAVITY DISTRIBUTION CURVES FOR POINTS HAVING 20 PER CENT WITHIN  $\pm 0.10$  SPECIFIC GRAVITY

Figure 7, where the curves apparently do not represent exact points of equal difficulty. However, the degree of precision required becomes less as higher specific gravities are considered, because all processes closely approach 100 per cent efficiency for a separation at specific gravities of 1.90 to 2.00. This means that some error in finding the exact point of equal difficulty for two coals at high specific gravities is inconsequential, and comparisons accurate enough for all practical purposes might be expected from this one curve except for some coals differing greatly in washing characteristics. If this

point could be demonstrated it would reduce the comparisons of two coals to a simple matter of developing  $\pm 0.10$  specific gravity distribution curves and of determining equal points of difficulty by that method.

TABLE III

TABLE TESTS NO. P17 AND C5, FEED UNSIZED THROUGH 407 TON-CAP

PRODUCT	SPECIFIC GRAVITY AND ZONES*	WEIGHT	ASH†	CUMULATIVE WEIGHT	CUMULATIVE ASH†
		<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
Table test No. P17:					
Float-and-sink of feed.....	Under 1.38	47.8	5.7	47.8	5.7
	1.38-1.50	19.1	15.2	66.9	8.4
	1.50-1.70	13.2	29.8	80.1	11.9
	Over 1.70	19.9	65.6	100.0	22.6
Washed products.....	1-5	31.9	8.8	31.9	8.8
	6-10	29.6	10.9	61.5	9.8
	11-14	16.9	19.7	78.4	11.9
	15-17	3.4	34.1	81.8	12.9
	18-19	2.1	48.5	83.9	13.8
	20-21	16.1	68.6	100.0	22.6
Table test No. C5:					
Float-and-sink of feed.....	Under 1.38	72.8	7.0	72.8	7.0
	1.38-1.50	13.3	20.2	86.1	9.0
	1.50-1.70	6.5	34.5	92.6	10.8
	Over 1.70	7.4	67.1	100.0	15.0
Washed products.....	1-2	2.8	8.5	2.8	8.5
	3-4	12.3	8.0	15.1	8.1
	5-6	18.3	8.9	33.4	8.5
	7-8	21.1	9.3	54.5	8.8
	9-10	18.0	9.3	72.5	8.9
	11-12	10.6	10.4	83.1	9.1
	13-14-15	3.5	18.1	86.6	9.5
	16-17	1.6	24.9	88.2	9.8
	18-19	3.2	34.2	91.4	10.6
	20-21	8.6	61.3	100.0	15.0

\* One-foot zones.

† Moisture-free basis.

Some test of this method of using the interval of  $\pm 0.10$  specific gravity to find points of equal difficulty was sought from which results obtainable by washing could be predicted and then com-

pared with those actually obtained. Such a comparison is difficult to make, as a moment's consideration will show. For the tests to be of value, the coals used should differ markedly in washing characteristics as shown by the float-and-sink separation, but should not differ materially in size and shape of particles, which must be considered separately from specific gravity. The apparatus used should be identical, the operators of equal skill, the tonnage the same, the methods of conducting and working up the two tests alike in every particular, and finally the results should represent equally good work.

Only two tests fully meeting the requirements could be found in the data available and even then the coals did not differ as much in

TABLE IV  
TABLE ADJUSTMENTS

CONDITION OF OPERATION	TEST NO. P17	TEST NO. C5
Coal washed per hour, tons.....	4.7 *	4.9
Length of stroke, inches.....	1.25*	1.0
Strokes per minute.....	258	268
Cross-slope, inches per foot.....	1.08	1.08
Elevation of refuse end of supporting channels above other end, inches.....	4.12	3.22
Average pulp ratio: $\frac{\text{Weight of water}}{\text{Weight of coal}}$ .....	2.05	2.30
Maximum height of high riffles, inches.....	1.25	1.00
Spacing of high riffles, inches.....	5.0	2.50

\* This length of stroke proved too long for continuous service.

washing characteristics as was desirable where only one comparison free from important assumptions was possible. The tests were made on coal-washing tables with the coals shown in Tables III and IV and in Figures 10 and 11.

These data will be clear without extended explanation. The float-and-sink data and curves have been calculated as explained earlier. The products of the table test have been handled in exactly the same manner both as to calculations of the data and construction of the curves. The washed products curves are simply curves of cumulative weight per cent against cumulative ash per cent and show the average ash content of the washed coal at any given yield per cent. The efficiency curves are obtained by dividing the yield

per cent shown by the table at any given ash content by the yield shown by the float-and-sink for the same ash content. If the table in making a washed coal containing 9.0 per cent ash recovers 93 per

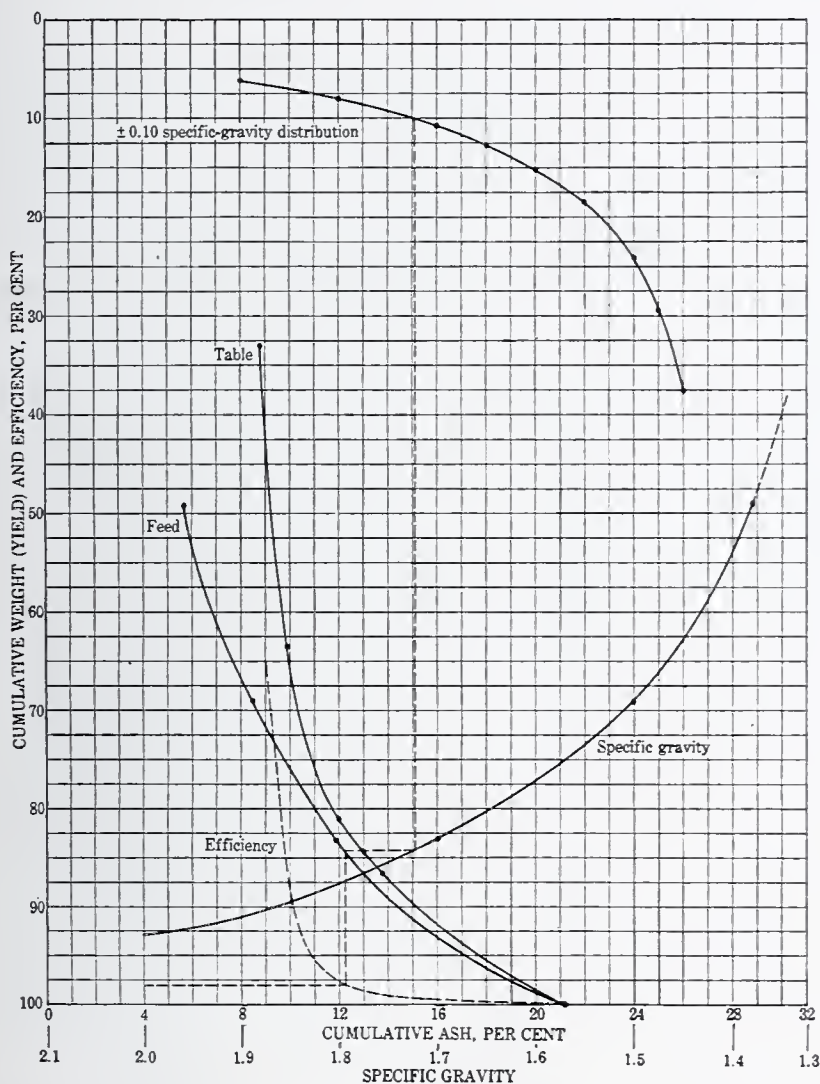


FIG. 10. TABLE TEST NO. P17, SHOWING RELATION OF  $\pm 0.10$  SPECIFIC GRAVITY DISTRIBUTION CURVE TO EFFICIENCY BY WASHING

cent of what the cumulative curve of the float-and-sink shows, its efficiency at that point is 93 per cent. The coals both contain a shale that slimes badly in water and both have about equal proportions of

flaky impurities; they differ mainly in particulars shown by float-and-sink separations. The coal in P17 was higher in ash content than in C5, 22.6 per cent as against 15.0 per cent, and had larger

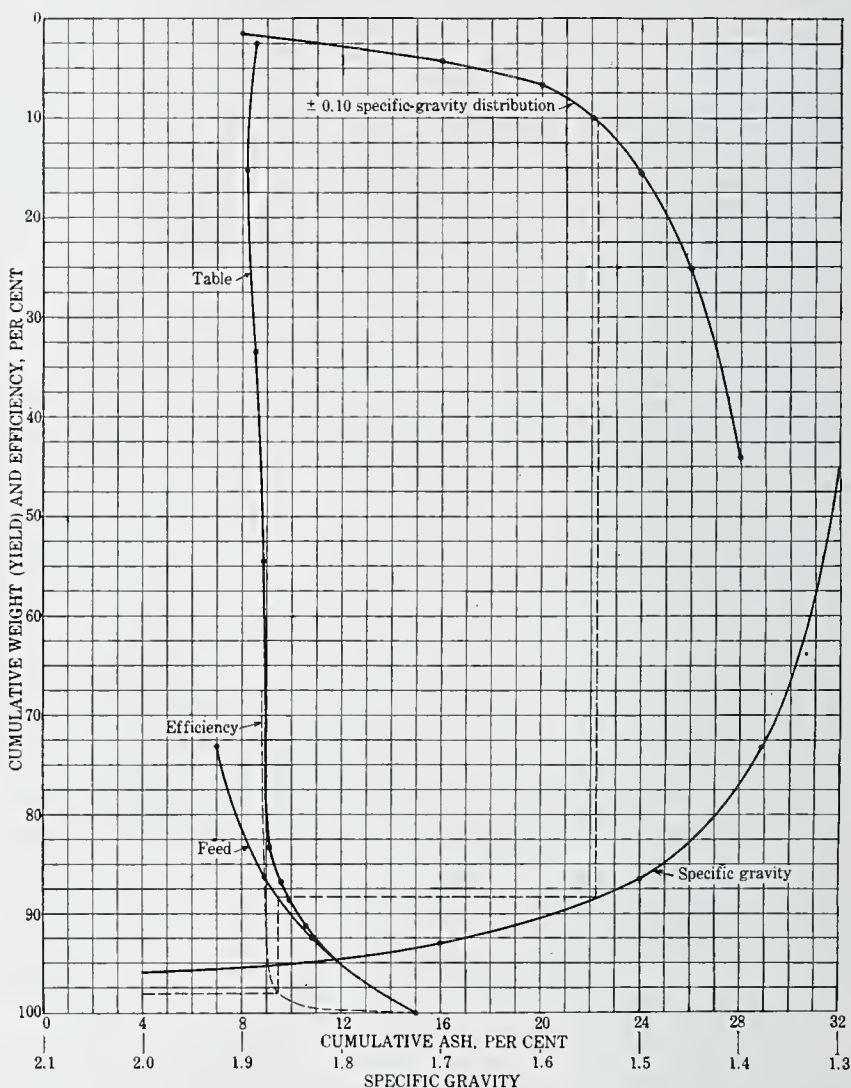


FIG. 11. TABLE TEST NO. C5, SHOWING RELATION OF  $\pm 0.10$  SPECIFIC GRAVITY DISTRIBUTION CURVE TO EFFICIENCY BY WASHING

proportions of bone in the fractions between 1.38 and 1.70, 32.3 per cent as against 19.8 per cent. The details of the test were essentially the same. The same table equipped with the high riffles

developed at the Northwest Experiment Station was used in both tests,<sup>3</sup> but Table 4 shows that in test No. P17 the maximum height of riffles was  $1\frac{1}{4}$  inches and in test No. C5 it was 1 inch. However, the slight advantage thus given P17 was balanced by the advantage held by test No. C5 in having closer spacings of the riffles. The quantity washed per hour was 4.9 tons as against 4.7 tons. The methods of conducting the tests were the same, and the adjustments of the tables were nearly enough the same for practical purposes. The distribution of products discharged from the table, which is a factor of great importance to table efficiency, was excellent in both tests. For maximum efficiency 2 to 3 per cent should be discharged in the first foot along the deck nearest the head motion and 27 to 30 per cent along the first 5 feet. The size of the remaining washed products discharged on the long side of the deck should then taper off uniformly so that a small proportion comes over the middling corner of the table. As this distribution is essentially that obtained in the table tests, they may be considered to represent excellent tabling and to be comparative. In order to facilitate comparison of these tests, percentages for a number of points on the two  $\pm 0.10$  specific gravity distribution curves in Figures 10 and 11 have been carefully read from the pencil curves for accuracy and are given completely in Table 5. For the sake of illustration the same point will be followed through each set of curves by means of a dashed line. If 10 per cent is found on  $\pm 0.10$  specific gravity distribution curve at the top of Figure 10 and is followed down to the specific gravity curve, it is seen to correspond to 1.723 specific gravity read at the bottom and to 84.2 per cent yield read at the left; if the dashed line is followed to the left to the cumulative float-and-sink curve, it is seen to correspond to an ash content of 12.4 per cent read at the bottom and to an efficiency of 98.0 per cent read at the left. If a point in Figure 11 is followed through as indicated by the dashed line, it is also found to end at an efficiency of 98.0 per cent. If a series of points are carried through from each  $\pm 0.10$  specific gravity distribution curve, the results obtained are those shown in the two right-hand columns of Table V.

The efficiencies predicted and those obtained all agree well; the maximum difference where the curves have any significance is 1.0 per cent, which is almost within the error of reading the curves. The

<sup>3</sup> Bird, Byron M., Coal-Washing Research Will Save and Better Coal While Increasing Capacity. *Coal Age*, 1927, vol. 31, p. 670.

point at 8.5 per cent ash, where the efficiency of test No. C5 is dropping off so rapidly, need not be considered because the slightest change of table adjustment would have materially altered the result. Thus by use of specific gravity distribution curves the efficiencies obtained in C5 could have been predicted from P17, made several years before, within the accuracy of reading from the curves. As efficiency at any given ash content is 100 times the yield of washed coal divided by the yield by float-and-sink at the same ash content, the efficiency curve once constructed can be applied to the float-and-sink curve to give the washed products curve.

TABLE V

VALUES OBTAINED FROM FIGURES 10 AND 11, SHOWING RELATIONSHIP OF  $\pm 0.10$  SPECIFIC GRAVITY DISTRIBUTION CURVE TO EFFICIENCY BY WASHING IN TABLE TESTS  
No. C5 AND P17

CUMULATIVE WEIGHT	SPECIFIC GRAVITY		YIELD BY FLOAT-AND-SINK		CUMULATIVE ASH		EFFICIENCY	
	Test No. C5	Test No. P17	Test No. C5	Test No. P17	Test No. C5	Test No. P17	Test No. C5	Test No. P17
<i>per cent</i>			<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
20	1.470	1.535	84.0	72.3	8.5	9.1	40.0	72.3
18	1.480	1.555	84.8	73.9	8.7	9.4	80.0	80.0
16	1.490	1.585	85.6	76.1	8.8	10.0	87.0	87.5
15	1.497	1.600	86.0	77.1	8.9	10.2	88.5	89.5
13	1.513	1.640	87.1	79.9	9.2	10.9	95.5	94.8
10	1.545	1.727	88.6	84.4	9.5	12.4	98.0	98.0
7	1.593	1.850	90.2	89.1	10.0	14.3	98.7	98.8

The method of applying from one coal to another the results of the separation according to specific gravity will doubtless be entirely clear from what has been given in the preceding discussion; however, it may be well to enumerate the various steps in order. Suppose that a new coal is to be washed to 10 per cent ash. The yield per cent corresponding to this ash content is read from the cumulative float-and-sink curve. Next, the specific gravity corresponding to that yield is read on the specific gravity curve. In turn the percentage of material within  $\pm 0.10$  specific gravity is read on the top curve. This percentage is applied to the  $\pm 0.10$  distribution curve of a known coal. The point so located is followed successively to the specific gravity curve, to the float-and-sink cumulative curve, and to the

efficiency curve. The efficiency thus determined, so far as specific gravities of coal and impurities determine the results, should be attainable on the new coal.

In many instances complete efficiency curves such as shown in Figures 10 and 11 will not be available, and the efficiency will be known for only one point on the  $\pm 0.10$  specific gravity distribution curve. If the curve shows that the specific gravity separation is more difficult than that of the new coal, obviously the same or higher efficiency may be expected on the new coal. But if the reverse is true, no prediction of results is possible. The data are simply insufficient. No prediction is possible as to what may happen in washing by any process when a more difficult separation must be made than the one on which data are available. The curves in Figures 5 and 6 have shown this to be a fact. The two washed products curves in Figures 10 and 11 also illustrate this point very well. As a washed coal of lower ash content was produced in those table tests, a greater spread occurred between the actual results obtained in washing and those shown to be possible by float-and-sink, with resulting decrease in efficiency.

#### *Evaluation of Variations in Size and Shape of Particles*

There are a number of systems of washing for which the results based on the specific gravity separation can be compared without any adjustments for size and shape of particles of coal and impurities. These are systems that, if a greater or less number of the various washing units are installed, can cope with any combination of specific gravities, sizes and shapes of particles. A number of examples of such systems could be enumerated but to avoid any controversial point, only one will be given. This system uses jigs to clean closely-sized feeds, say in the range from 3 inches to  $\frac{1}{4}$  inch sizes; tables on feeds that have been classified in hydraulic classifiers for the sizes from  $\frac{1}{4}$  inch to about 65-mesh; and froth flotation for the material through 65-mesh. The sized feeds to the jigs render them practically independent of shape of particles of coal and impurities. The classification of the coal through the  $\frac{1}{4}$  inch size, followed by tabling of the products of the classifier, enables the two together to take care of any combination of size and shape of particles over the range from  $\frac{1}{4}$ -inch to about 65-mesh. Flotation, so far as is known, is largely independent of size and shape of particles so long as the particles are fine. Results of such a complete washing system and others

like it can be compared directly by use of the specific gravity distribution curves.

When a washing system is abridged in some way, then other factors such as size and shape of particles of coal and impurities must be carefully considered to see if they are comparative. If they are not comparative the corrections to apply for all different processes will be too involved for explanation in a short paper. But some examples of the method of arriving at the corrections for the jig-table-flotation system of washing will exemplify the proper procedure. Suppose froth flotation is omitted from the system just mentioned. Since an inadequate method is provided for cleaning the extremely fine sizes, the proportion of shale that will probably slime in water must be carefully compared for the two coals under consideration. Although it is true that preliminary classification of the feed to tables enables them efficiently to wash sizes down to about 300-mesh, it is simpler to disregard this fact and assume that the sizes through 65-mesh are not cleaned by the tables. With this assumption the results shown by the specific gravity distribution curves are corrected by adding to or deducting from the yield of washed products for the new coal the difference in the amount of unwashed fines present. Whether to add or to subtract depends upon the circumstances. If the fines are to be thrown away, the amount may be subtracted; if they will ultimately end in the cleaned coal they should be added in an unwashed condition.

The next natural abridgment of the above flow sheet is the omission of the classifier,<sup>4</sup> for it is a new method of cleaning coal. If this is done, the relative sizes of the particles of coal and impurities in the two coals should be compared, because a feed consisting of coarse particles of bone and fine particles of coal has been found hard to table to a low ash content.<sup>5</sup> Any marked variations in this particular, however, would be unusual in a raw coal; variations are likely to be found in intermediate products that are being rewashed after crushing. Similarly, the two coals should be compared for the presence of thin pieces of bone of low specific gravity. If one coal has more

<sup>4</sup> Bird, B. M., and Yancey, H. F., Hindered-Settling Classification of Feed to Coal-Washing Tables. Tech. Pub. 76, Amer. Inst. Min. and Met. Eng., 1928. Re-treating Middlings from Coal-Washing Tables by Hindered-Settling Classification. Tech. Pub. 77, Amer. Inst. Min. and Met. Eng., 1928.

<sup>5</sup> Bird, B. M., Sizing Action of a Coal-Washing Table. Rept. of Investigations, Bureau of Mines, Serial 2755, 1926, 8 pp.

of this material than the other, some factor of safety should be applied to yields determined by specific gravity distribution curves. Probably a 5 or 10 per cent lower efficiency than shown on the known coal should be taken for the proportion of the total raw coal cleaned by tables. Of course, in addition, any corrections previously made for slimes should be made here also.

A still more common abridgment of the complete flowsheet is to wash in the jigs all sizes from 1-inch down in one operation. If washing results so obtained are to be used to predict what results may be expected on another coal, then, as the system is not complete enough to clean the fine sizes in a very efficient manner, the coals should be compared to see how the characters of the coals through 10 or 20 mesh compare. If the coals differ materially, some correction is necessary; exactly what this should be is difficult to say. A jig will do surprisingly good work on an unsized feed if the degree of pulsion and suction is carefully regulated and if the jig is run at one-half to two-thirds of its rated capacity. Probably a change in the tonnage proposed for the washers would take care of all ordinary variations between unsized feeds from 1-inch and smaller. This same method will also care for variations in the proportions of thin flakes of bone in the two coals. A distinct suction stroke and a fully mobile bed on the pulsion stroke will do marvels in removing that sort of material with jigs. In the treatment of slack sizes any differences in the sizes through about 20-mesh should be added or subtracted as was done before for the material through 60-mesh.

If the flowsheet is still further abridged to include only jigs to clean all sizes from 3-inch to 0-inch in one operation, the operator wishing to make comparisons from one plant to another must be very careful if the data of the two coals show the sizes through  $\frac{1}{4}$  inch to be very much different in quantity or character. Experience has shown that if a jig washing coal of 3-inch to 0-inch is adjusted to clean the fine sizes, it wastes coarse coal; and if it is adjusted for the coarse sizes, it will do very inefficient work on the sizes below  $\frac{1}{4}$ -inch. The correction would be to add or subtract the difference in fine slack to the washed coal, assuming an efficiency of washing of about 30 or 40 per cent.

These few brief notes illustrate the method of adjusting the yields of washed products. The same general mode of study can be applied to any other process that is abridged. The sizes that are not cleaned by the incomplete process should be noted and the two coals com-

pared to see whether those sizes are markedly different. If so, some ample correction must be applied to the results predicted by use of the specific gravity distribution curves. The amount and character of this can only be determined by studying the process in question.

After an operator has applied to the washing of new coal the results obtained from some plant actually operating or has compared such results with results being obtained in his own plant, he will be desirous of determining whether the best work with that process is represented, and, if he is washing his own coal, whether he is getting the most out of his own plant. Such a determination is difficult to make, but is none the less valuable. The efficiency of an operation depends upon two large factors, the correctness of the installation and the skill of operation. Both of these can be judged to some extent by studying any washery operation. There are, so to speak, some criteria of a good plant and of good operating methods.

Every plant has a certain number of washing units, motors, conveying systems, and the like. The distinctions between plants are in what might be called the "trimmings." The trimmings of a plant are parts of it that are not absolutely essential to the washing of coal. They consist of good light, both natural and artificial; excess washer capacity so that the washers never need to be crowded; good feeders that deliver a uniform tonnage of coal to the washers; large equalizing bins between mine and washery and in the washery proper to take care of temporary overloads; a system of tanks to maintain uniform water pressure to all washers; automatic samplers on feed and washed products; excess screen area on screens to take care of emergency conditions; variable-speed motors on dewatering elevators to permit of running the buckets entirely full of coal; an adequate water clarification system; and many like details that might be named. These are the items that mark the difference between good and poor construction; their presence or absence inevitably influences the results.

Skill of operation is the more important element in good coal washing; without it a well-designed plant is of no value. The following are some indications of skillful operation: The constant daily use of the float-and-sink test to adjust the washers and to check their efficiencies; daily, weekly and monthly checks of the yields of washed coal on a dry basis; frequent determinations of efficiency by comparisons of these figures with the yields obtained by float-and-sink

tests of the raw coal; the condition of essential parts of the washers, such as the riffing of tables and the tightness of jig plungers and the like; the uniformity of the operation as a whole, as for example, the uniformity of drawing the refuse from the jigs, or the uniformity of the water distribution on the tables; and many like elements that contribute much to good results.

No adjustment of results is possible either for the correctness of installation or for the skill of operation, but such information as the operator can obtain by visiting other plants will indicate to him the reliance he may place upon their results. Or, if he is comparing the results obtained in his own plant with those of another plant such information will guide him as to whether poorer results are due to the failure to install a sufficient number of "trimmings," to poor operation, or to some inherent weakness of the process.

## FACTORS IN DESIGN OF COAL CLEANING PLANTS

By JAMES B. MORROW

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The paper by Dr. Glintz has discussed the fundamentals of the coal cleaning problem and the nature of the results that it is desired to accomplish. Mr. Bird has taken up the matter of the necessary testing to determine the characteristics of the coal to be treated, so it does not seem necessary to discuss those phases of the question any further, but the writer will take up some phases of the actual design of the operating plant.

The use of the finished product is one of the most important factors influencing the plant design, as today we do not have any definite standards as to what constitutes a clean coal, and for this reason it is very difficult to make any definite comparison between various methods. For some purposes, it is enough to take out only the larger part of the true rock and for others, all of the rock must be removed and also a part of the middling or bony product.

Until a few years ago, we were only concerned with the removal of ash and sulphur but lately we seem to find an opinion that the non-coking compounds, such as the fusains and mineral charcoals, have just as bad an effect on coke structure as the presence of free shale or rock and investigations are now being conducted on this phase of the cleaning problem. The fusion points of the clean coal ash is also becoming a more important factor as there are certain markets which are more interested in a high fusion point of ash and freedom from extraneous impurities than they are in the inherent ash of the coal itself. To a certain extent, this element is also related to the removal of the fusains, as on the Pittsburgh Seam at least, they seem to be of uniformly low fusing point due to the high lime content, which runs from 40 to 50 per cent in the ash. Uniformity of product is also becoming more important as the coal trade becomes more interested in determining the true value of the product. The cleaning plant located at one particular mine can certainly have a simpler flow sheet than the central plant treating products from a group of mines in which there may be considerable variations in the characteristics of the raw product.

The nature of the separation that it is desired to make is certainly

one of the principal factors governing the design and it does not seem to the writer that sufficient emphasis has been given to the point that a separation at a 1.40 gravity is an entirely different matter than a separation at a 1.70 gravity and yet there are many cases where the 1.70 gravity separation will not produce the desired quality of product for some particular market. There are quite a number of machines or processes available today that will make a satisfactory separation at a high gravity and with a reasonable degree of efficiency but when operating on a low gravity and still maintaining a high efficiency, it is an entirely different problem. The roughing job as it might be called, is naturally a lower cost plant than the finer separation and there is no doubt but that there are many cases where it would be economically wrong to put in any higher cost plant than is necessary to prepare the coal for the particular market for which it is intended. One of the principal reasons for the higher cost of the low gravity separation is in the lower tonnage that can be handled on the same unit. For instance, in the case of a particularly bony coal, a three-cell jig will give a very satisfactory separation with a capacity of 75 tons per hour at a 1.75 gravity but when operating at a 1.40 gravity, it is necessary to reduce the tonnage to 50 tons per hour, in order to make a satisfactory separation of the clean coal and at the same time, the loss in the refuse will increase. Also the design of the water settling system is of considerably more importance in low gravity washing.

In order to discuss the variations that may be encountered in the design of cleaning plants in general and wet washing plants in particular, it might be well at this time to endeavor to make an analysis of the various elements which go to make up a complete preparation plant, for it is very obvious that the cleaning unit in itself does not necessarily constitute a complete coal preparation plant and it may be of some interest to point out the effect of the percentage cost of the various auxiliary units as compared to the plant as a whole.

*Raw Coal Feed.* The delivery of the raw coal to the point where the cleaning unit starts to function is one of the biggest variables connected with the plant layout and is subject to almost any number of modifications. In some cases, this unit may just represent a conveyor or elevator from the tippie to the plant and in its simplest form it is not such an important element of the cost. However, when the raw coal is first stored in bins with mixing arrangements to maintain a uniform quality of material going to the cleaning plant, this may then become one of the largest factors in the cost of the completed plant.

*Actual Units That Are Performing the Cleaning Operation.* Among the most common of these in American practice today are air tables, wet jigs and tables, the Chance cone and the Rheolaveur, and the choice of the particular process to be used at this point, depends more on the character of separation that is desired and this is largely determined by market conditions and here it might be well to state again that the cost of these units will vary considerably with the specific gravity at which it is desired to operate.

*Screening and Sizing of the Cleaned Product.* This again is a feature which is subject to a wide variation depending upon whether the plant is washing coal from 4-inch down and screening the finished product into say four sizes or whether the plant is operating on slack coal and loading an unsized product, as is the most common condition in plants that are handling coal for coking purposes, in which latter case there may not even be any screening at all.

*Loading and Mixing.* This factor is again subject to a wide variation depending on the nature of the mixing facilities that may or may not be provided and as to whether the sized coal is handled on booms.

*Disposal of Refuse.* This factor is again subject to a wide variation in cost. In the simplest case, the refuse will be discharged into a bin outside of the washer and loaded out in railroad cars. In other cases, it may be necessary to provide an aerial tram or possibly some form of hillside dump.

*Mechanical Drying and Filtering.* Possibly this factor is subject to wider variations than any other units in the mill as in some cases there will not be any attempt at drying other than natural drainage in the bins and in others it may be absolutely necessary to use centrifugal dryers and filters in order to reduce the moisture to a satisfactory point to meet market conditions. There is no question but that this is one of the main drawbacks of any wet washing system and an item that is going to demand more serious consideration in the future than it has had in the past.

*The Circulating Water System.* Perhaps this item is not so much subject to such extreme variations as the other elements previously mentioned, except as the quantity of circulating water may be higher in some systems than in others but even then we might expect this particular item to be reasonably consistent as regards its percentage of the total cost.

*Sludge Recovery.* This includes the necessary tanks or thickeners

for settling out the fine coal and returning the overflow water to circulation. It may vary widely in the different districts depending on whether a part or all of the water carrying the fine coal is allowed to go to waste or as to whether the plant is operated on a locked system with no waste of water and complete recovery on the fine coal. If all or part of the sludge is permitted to go to waste there is a certain loss in the fine product which, at least in a large tonnage plant, can hardly be justified.

*Washery Structure.* This is subject to some variation depending on the type of construction used and also on the fact that some systems may require considerably more space than others but I do not believe that it is ordinarily such a serious item when it comes to comparing the costs of different methods of washing, provided that the same standards are maintained for each method.

*Laboratory, Repair Shop and Automatic Sampling.* These are, of course, subject to variation depending on what it is desired to do in this respect. In the past automatic sampling does not seem to have received the attention that it deserves for it is certainly of vital importance in maintaining uniformity in the operating results.

It is manifestly impossible to make any definite statement as to what should be the relative percentage of the total cost of these various items but for purposes of illustration, I would present the following figures as being a reasonably accurate statement of what might be termed a normal condition for a complete wet preparation plant handling coal 4 inches and under with full facilities for screening, mixing and loading four different sizes, with facilities for centrifugal drying and filtering of the fine coal and having an approximate capacity of 350 tons an hour on low gravity separation and 500 tons an hour on a high gravity separation.

*Raw Coal Feed.* For the raw coal conveyor, we have taken a simple case of conveying from a bin into the washer but not including the cost of the bin and with a magnet for removing tramp iron. This amounts to 6.3 per cent of the total cost.

*Cleaning Units.* For the cleaning system, we have assumed a complete Rheolaveur plant with coarse and fine coal units and the necessary recrushing of middlings and screening of the tailings. This includes the cost of all launders, boxes, elevators and platework motors and drives and auxiliary machinery from the time the coal is delivered into the cleaning units, up to the point of delivery of the cleaned product to the screens and of the refuse into an elevator

sump. The total cost of these items will be approximately 21 per cent of the total plant cost.

*Wet Screening.* The screening of minus 4 inches coal into four sizes with ample screen surface for dewatering of the screened product, would amount to 5.2 per cent of the total plant cost. It should be noted that at this point the dewatering increases the normal screening cost.

*Loading.* The cost of a complete loading station with loading booms on the sizes above 1 inch together with the necessary structure and arrangements for mixing in any desired proportions, will amount to 8.3 per cent of the total plant cost.

*Refuse Disposal.* For this element, we have assumed a very simple case in which the refuse is discharged into an elevator boot and from thence elevated to a storage tank directly outside of the building, arranged for direct loading into railroad cars. Such an installation amounts to 3.8 per cent of the total cost.

*Drying.* For this element, we have assumed centrifugal drying of approximately 130 tons per hour of minus  $\frac{3}{8}$  inch product with a spare drying unit and the necessary conveyors to deliver the coal to the dryers. Also the filtering of the fine coal sludge and delivery to the loading system. Such an installation will amount to 12.5 per cent of the total cost.

*Water Circulating System.* This includes the pumps and piping and the necessary collecting sumps for the water circulating system. This item amounts to 7.3 per cent of the total cost.

*Sludge Recovery.* The settling of the sludge in a Dorr thickener with the return of the overflow water to the circulating system and the pumping of the sludge to the filter, will amount to 6.5 per cent of the total cost. It should be noted here that this system provides for no waste of water.

*Structure.* For this unit, we have assumed a steel building with concrete columns and curtain walls up to the first floor, a cement tile roof and asbestos metal siding together with the necessary provisions for the heating and lighting of the structure. A building of this nature will amount to 25 per cent of the total plant cost.

The other accessories such as the laboratory, repair shop and automatic sampling, under average conditions, can be taken at about 4.1 per cent of the total cost.

The following is a list of the various items and their relative percentage of the total cost:

	<i>per cent</i>
Raw coal.....	6.3
Cleaning units.....	21.0
Wet screening.....	5.2
Loading.....	8.3
Refuse.....	3.8
Drying.....	12.5
Piping.....	7.3
Sludge.....	6.5
Structure.....	25.0
Laboratory—shop.....	4.1

In considering these figures, it should be noted that they are representative only of a very complete type of coal preparation plant with full facilities for screening, mixing and loading and perhaps a little unusual care in the drying of the fine coal. They are based on the use of first class materials and construction throughout and designed with a view of a low operating cost rather than a low first cost. They do not include any allowance for the trackage, sub-station or office building.

My idea in presenting this data has been to show how nearly impossible it is to make any general statement as to the cost per ton hour of a washing plant as I believe that it will be readily seen that there is a possibility for greater variations in the cost of the coal handling equipment than in the cost of the cleaning unit itself. In other words, the functions of screening, loading, mixing, drying and sludge recovery are more a function of the plant as a whole than they are of any particular wet washing system and it will be noted that in the particular example given, these units will total to 33.5 per cent of the total plant cost as compared with 21 per cent for the actual cleaning units.

I believe these figures will show that for a complete plant handling a large tonnage, that the efficiency of the separation is one of the most important factors, as a saving of only 5 per cent of coal in the refuse on double shift operation for three hundred days a year, for a 500 tons per hour input and 10 per cent of refuse, will amount to over \$20,000 a year or one-fifth of the original cost of the entire cleaning units.

In closing, I would like to say that while I have used comparative figures and costs of wet washing plants, it is only on account of the fact that I happen to have more accurate information on the detailed costs of the units in a wet plant than in a dry plant. However, after

some little experience with the operation of a dry cleaning plant, I feel that there is no question but what on certain coals and operating at a relatively high gravity, that the dry process can be made to give a very satisfactory separation on certain types of coals and while it would rather seem that in the present stage of development that the dry process is not as well adapted to the low gravity separations as several wet processes, at least we do not have to contend with the drying of wet coal and perhaps the dust problem which replaces it is now getting to the point where it is not so serious a difficulty as it has been in the past. The advantage of a dry product is a very real one for certain markets and in many cases will offset the lower efficiency of the process, particularly in cases where it is only necessary to remove a small percentage of refuse.

#### DISCUSSION

CHAIRMAN NEALE (Pittsburgh Coal Company, Pittsburgh, Pa.): We have a few minutes left before we must adjourn. This, I think, is the largest gathering of coal cleaning experts I have ever seen in this country. I see in the audience advocates of the different processes of coal cleaning, and I think there should be some very interesting discussions. We will discuss Mr. France's paper first.

GODFREY M. S. TAIT (Consulting Engineer, Washington, D. C.): In connection with Mr. France's paper, I wish to call attention to the fact that the data is probably based upon French practice, and that the improvements in the washing tables operated by air practically cover all the disadvantageous points that were alluded to.

For example, it is not necessary any more to remove dust. It is also not necessary in some of the processes to size the coal before cleaning. In some cases one table will handle all sizes. That puts an entirely different aspect on the proposition and I think for the records of the American practice we should bear that in mind.

The figures on air cleaning may be of interest. For example, on Pittsburgh coal going over the tables 7 inches to nothing; and the raw coal having 11.2 per cent ash, 1.9 per cent sulphur, and the theoretical reduction down to 7.5 per cent ash, according to the washability tests, the actual results were, ash reduced to 7.9 per cent and sulphur to 1.7 per cent.

DR. BARTEL GRANIGG (Hochschulprofessor, Leoben): The Rheolaveur Process requires no machinery and is based upon the gravity filter, but I do not think the gravity filter is always necessary. We have other fields at our disposal.

For a long time I have been working on processes separating materials based on the fact that these materials are flowing through fields with alternating currents of 16 cycles and of 500, of 2,000 or more than 100,000 cycles,

and I finish by sending the materials through fields by electrolytic waves like radio waves. My experience convinces me that we have a large field to use.

We see here opportunities to work out new methods for separating materials. I believe that later on I shall have an opportunity to explain to you these new methods of separating materials based upon electric properties.

T. M. CHANCE (H. M. Chance & Company Philadelphia, Pa.): I think that we were all much interested in the paper that Mr. France has presented. I believe that European engineers have done much to translate the art of coal washing from a craft to an engineering basis.

However, I am sorry that there has been a tendency to the discussion of Mr. France's paper to bring in the question of the relative merits per se of the dry cleaning and the wet cleaning processes because, as Mr. Bird so ably illustrated, it is hardly probable that any one system will fit every condition in its entirety. I believe that the future history of the washing of coal will duplicate that of the development of our present prime movers and that it will be found that a number of systems differing quite radically in physical characteristics will survive in the different fields, just as prime movers driven by gas, oil and steam show every tendency to survive in competition both with each other and with prime movers driven by water power.

CHARLES ENZIAN (Berwind White Coal Mining Company, Windber, Pa.): I made a few notes on Mr. France's paper and I was sorry in one respect, that the over-all efficiency equation formula was omitted. It will be sometime before the paper will be available and I think some very valuable time may be lost.

I was wondering whether Mr. Campbell would not state his formula of the ratio of practical efficiency to the theoretical efficiency from the float and sink studies of Rheolaveur, and make some direct reference as to the inefficiency of sulphur reduction in the dry process compared with the wet process.

I might state that practical experience for over two years in air cleaning plants does not quite bear out the broad assertion that the wet system is superior to the dry system.

Relative to the operating costs, there is some question whether the various units that Mr. Morrow explained would have to be manned and operated by more skilled men in a wet system as compared with the dry system.

I am under the impression that the academic discussion of the relative loss of heating value of coal prepared by a wet system over a dry system will bear revision.

The question of handling and marketing a wet product as compared with a dry product is a very serious one, especially where unloading facilities of a customer are restricted. I gather the impression that the premises of the paper assumed that the reduction starter of ash, was in reality the sulphur reduction. From the stated figures, I have gained the impression that they have a much wider range of ash and sulphur reduction than we have in Pennsylvania coal.

ANDREW ALLEN (Allen & Garcia Company, Chicago, Ill.): There is one important fact in connection with the Rheolaveur that should be emphasized in connection with this and other processes. Mr. France has started with the simplest apparatus of classification, namely, a flowing stream which, as embodied in the launder, has been in use since the days of Archimedes. The launder offered great possibilities on account of its simplicity and its ability to handle a great range of sizes; but it had never before been harnessed so as to make an efficient separation. The launder was always capable of yielding a pure primary product off the top, but no one had ever been able to extract a pure refuse continuously or to handle the middlings.

From this beginning, Mr. France has developed a process capable of producing not only a good coal but a good refuse and also handling most efficiently the materials of intermediate gravity. The development of recirculation and the continuous removal of refuse has made a very perfect process out of what was originally a very crude apparatus.

What Mr. France has done with the launder is in my opinion the most important contribution of modern times to the art of washing coal. His application of the launder will be followed by similar improvements of processes built around other machines. Any machine capable of yielding a pure product without too much presizing is capable of development into an efficient process by use of the principles of progressive concentration and re-circulation. Both jigs and air tables are handling a much greater range of sizes than would have been thought possible a few years ago and are thus capable of further development on these lines.

I wanted to bring out this point as strongly as possible, as I believe the main thing in any washing plant is the *process* developed around a machine which will handle material with little or no presizing.

CHAIRMAN NEALE: Are there any further questions? If not, we will pass to the discussion of Mr. Bird's paper.

JAMES R. CAMPBELL: The writer has made several contributions to the literature on the subject of coal washing in the United States within the past few years and has called particular attention to formulating the washing results by means of standard efficiency formulas, but at no time has he made any attempt to define the washing gravity although the subject has been hinted at several times. In the first place, there is no such thing as washing gravity in any process of washing either by the wet or by the dry processes. All gravities are simulated gravities. There is one flotation process on the market, but even in this process, the gravity is an artificial gravity maintained by agitating a mixture of sand and water. Real gravities can only be obtained by making heavier than water solutions, and processes based on heavy density solutions have not proved to be a commercial success.

In any gravity process the washing gravity may be defined as that gravity at which by an interchange of sink in the washed coal with float in the refuse the quality of the washed coal is not impaired when the sinks and floats are expressed in the proper terms and express the correct relation to each other;

or practically, in efficient washing, it is that gravity at which, when the sink in the washed coal does not exceed 1 to 2 per cent the float in the refuse shall not exceed 2 to 5 per cent, the percentages being expressed as weights of themselves. These percentages must be calculated back to terms of feed coal in order to formulate the results. The washing gravity may be directly determined from the washability study of the feed coal and the basis is established by the ash or/and sulphur required in the washed coal. The washing gravity may be further defined by chemical analysis as follows:

$$\begin{aligned}\text{Washed coal} &= a + 0.5 \text{ per cent} \\ \text{Refuse} &= b - 3.5 \text{ per cent}\end{aligned}$$

where (a) equals the theoretical ash in the washed coal and (b) the theoretical ash in the refuse as determined by the washability study.

The writer has already called attention in several of his contributions to the fact that the old Drakeley's formulas are somewhat inadequate in formulating the qualitative and quantitative efficiencies of coal washers and has suggested some modifications. In none of these formulas has the character of the sink in the feed coal and the character of the sink in the washed coal been made a factor in formulating the qualitative efficiency. To those who are making sink and float tests for the evaluation of the performance of coal washers, it is very obvious that this is an important factor. It is very clear that washed coal with 2 per cent sink in it with 50 per cent ash is not as efficient a washer as one having 2 per cent sink in the washed coal with 40 per cent ash in the sink. For this reason it seems desirable to have the qualitative efficiency modified still further and based on interjecting the ash factor in the sink. For this purpose the writer suggests complete modified Drakeley's formulas as follows:

*Drakeley's Formulas (Modified)*

Qualitative efficiency =

$$(a) \quad 100 \times \frac{\% \text{ sink in feed coal} - (\% \text{ Recovery} \times \% \text{ sink in washed coal})}{\% \text{ sink in feed coal}}$$

$$(b) \quad 100 \times \frac{\left( \frac{\% \text{ sink in feed coal} \times \% \text{ ash in sink}}{\% \text{ sink in feed coal} \times \% \text{ ash in sink}} \right) - \left( \frac{\% \text{ Recovery} \times \% \text{ sink in washed coal} \times \% \text{ ash in sink}}{\% \text{ sink in feed coal} \times \% \text{ ash in sink}} \right)}{\% \text{ sink in feed coal} \times \% \text{ ash in sink}}$$

$$* \text{ Recovery} = 100\% - \% \text{ refuse.}$$

Quantitative efficiency =

$$100 - \frac{(\% \text{ refuse} \times \% \text{ refuse float})}{100}$$

$$\text{Bank Loss} = \frac{\% \text{ refuse} \times \% \text{ refuse float}}{100}$$

or  $100\% - \text{Quantitative Efficiency.}$

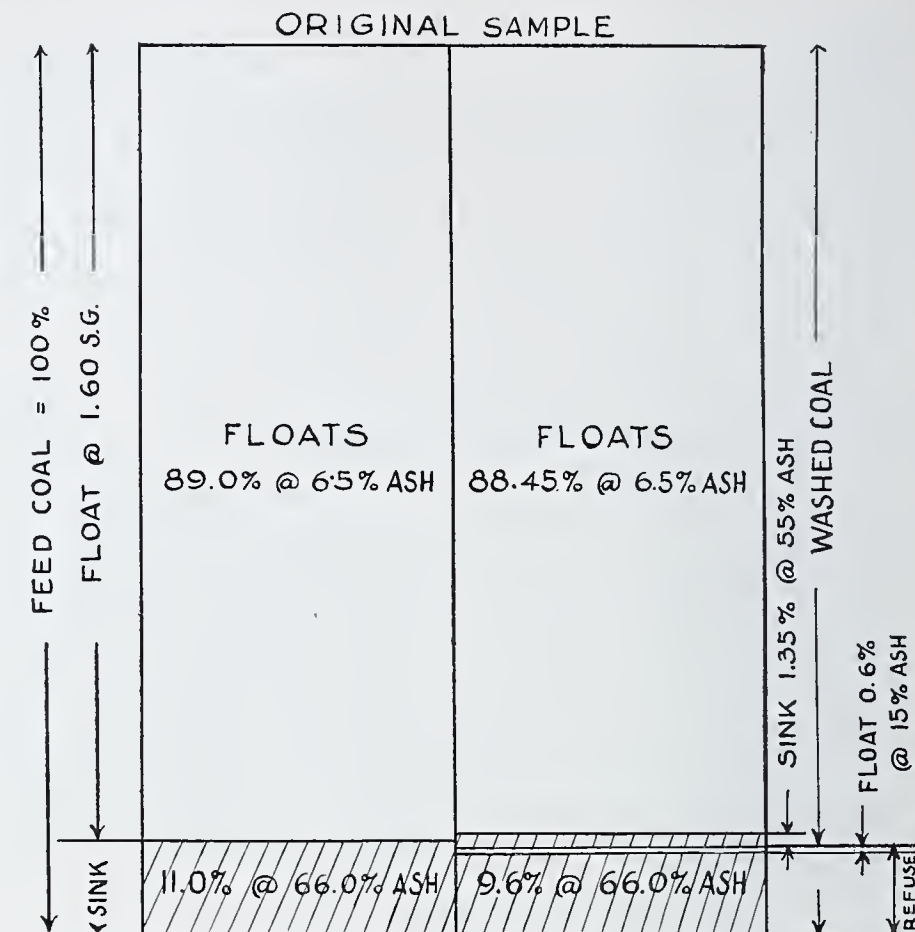


CHART I. GRAPHIC ANALYSIS OF SINK AND FLOAT DATA

*Separation analyses of individual samples*

Feed coal = 100 per cent

Float, 1.60 S.G. 89.0 per cent @ 6.5 per cent ash.

Sink, 1.60 S.G. 11.0 per cent @ 66.0 per cent ash.

Average = 13.0 per cent ash.

Washed coal = 89.8 per cent

Float, 1.60 S.G. 98.5 per cent @ 6.5 per cent ash.

Sink, 1.60 S.G. 1.5 per cent @ 55.0 per cent ash.

Average = 7.2 per cent ash.

Refuse = 10.2 per cent

Float, 1.60 S.G. 6.0 per cent @ 15.0 per cent ash.

Sink, 1.60 S.G. 94.0 per cent @ 66.0 per cent ash.

Average = 63.0 per cent ash.

*Sink and float in washed coal and refuse in feed coal percentages*

Floats, 88.45 per cent @ 6.5 per cent ash = 5.8 per cent ash in original sample

Sinks, 1.35 per cent @ 55.0 per cent ash = 0.7 per cent ash

Floats, 0.60 per cent @ 15.0 per cent ash = 0.1 per cent

Sinks, 9.60 per cent @ 66.0 per cent ash = 6.3 per cent

100.00 per cent	= 12.9 per cent ash in original sample
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(Legend continued at bottom of page 123)

The preceding formulas are exemplified as follows showing the difference in the qualitative efficiency by the two methods of calculation:

*Sink and float data—washing gravity 1.60:*

Feed coal sink.....	11.0 per cent
Ash in sink.....	66.0
Washed coal sink.....	1.5
Ash in sink.....(a)	55.0 (assumed)
Ash in sink.....(b)	40.0 (assumed)
Float in refuse.....	3.0
Recovery.....	89.8
Reject.....	10.2

*Qualitative efficiency =*

$$100 \times \frac{11.0 - (1.5 \times 89.8)}{11.0} = 87.7\% \text{ on Float and Sink basis only}$$

$$(a) 100 \times \frac{(11.0 \times 66.0) - (89.8 \times 1.5 \times 55.0)}{11.0 \times 66} = 90.0\% \text{ @ } 55\% \text{ ash in sink of washed coal}$$

$$(b) 100 \times \frac{(11.0 \times 66.0) - (89.8 \times 1.5 \times 40.0)}{11.0 \times 66.0} = 92.5\% \text{ @ } 40\% \text{ ash in sink of washed coal}$$

$$\text{Quantitative efficiency} = 100.0\% - 0.3\% = 99.7\%$$

$$\text{Bank Loss} = 0.3\%$$

Referring to the definition of washing gravity as given above, the writer gives the data in the chart on page 122 by way of exemplification. This chart and tabulation shows the effect of interchanging high ash sink in the washed coal with lower ash float in the refuse. In the standard sink and float data it will be noted that the ash in the washed coal is 7.2 per cent. It carried 1.5 per cent float with 55.0 per cent ash. On the basis of a complete interchange the ash in the washed product is 6.6 per cent showing a possible improvement of 0.6 per cent. It must be borne in mind, however, that a complete interchange is a 100 per cent job and not possible in operation. The main point is that the most efficient washer produces a minimum of low ash sink in the

*Combining floats of washed coal and refuse, also sinks of washed coal and refuse (interchanged)*

Floats:

$$\left. \begin{array}{l} \text{Washed coal } 88.45 \text{ per cent @ } 6.5 \text{ per cent ash} \\ \text{Refuse } 0.60 \text{ per cent @ } 15.0 \text{ per cent ash} \end{array} \right\} = 89.05 \text{ per cent @ } 5.9 \text{ per cent} = 6.6 \text{ per cent ash.}$$

Sinks:

$$\left. \begin{array}{l} \text{Washed coal } 1.35 \text{ per cent @ } 55.0 \text{ per cent ash} \\ \text{Refuse } 9.60 \text{ per cent @ } 66.0 \text{ per cent ash} \end{array} \right\} = 10.95 \text{ per cent @ } 7.0 \text{ per cent} = 63.9 \text{ per cent ash.}$$

---

100.00 per cent

---

100.00 per cent

## CHEMICAL TEST DATA

## WASHERY

Quantitative Efficiency = \_\_\_\_\_%

[illegible]

\* Washing gravity and testing gravity must be the same.

Remarks:

washed coal and a minimum of lower ash float in the refuse at the washing gravity showing that no rock is left in the washed coal and no free coal in the refuse. This must be true if the washer is efficient.

In the tabulation it will be noted that the normal recovery is 89.8 per cent and with a complete interchange it drops to 89.05 per cent showing a net loss in recovery of 0.75 per cent which is compensated for by the increase in the quality of the washed product. All these factors must be carefully considered when arriving at a conclusion on the performance of any coal washing job.

A convenient method for keeping a record of float and sink data is given on page 124.

T. M. CHANCE: I would like to subscribe entirely to Mr. Morrow's final analysis. We have found that the ratio of the cost of cleaning units to the entire cleaning plant will run from five to ten depending on the amount of auxiliary equipment required. Thus, where the cleaning unit itself costs but \$40,000 erected, the entire plant may cost from \$20,000 to \$40,000. Feed conveyors, loading booms and lump picking tables, cost just as much whether they are placed in an ordinary mine run tippie or in a plant producing nothing but mechanically cleaned coal and this feature has sometimes been lost sight of when considering what the over-all cost of any given plant will amount to.

In reference to removal of dust and the drying of fine coal. Plants requiring such equipment will naturally cost more than those that can be operated with a simpler layout and I think that every effort should be made to reduce the amount of such auxiliary machinery in the final plant. We therefor have endeavored to so lay out the plants that we have designed as to reduce the final coal problem as much as possible and this has not only resulted in securing a greater realization in the commercial sale of the coarser coal produced but also has permitted the installation of plants with a minimum of fine coal auxiliary equipment.

RAY W. ARMS (Robert & Schaefer Company): I would first of all like to refer to Mr. Bird's paper for a moment. I think he has brought out very clearly these specific things that one must know about a coal to compare the relative washability with some other coal. That is we have carelessly referred to it in the past as the "near gravity material" or more loosely still as "bone coal."

Mr. Bird's paper has shown a way to eliminate the large portion of very light coal and the large portion of very heavy refuse, which is the simple and primary A. B. C. cleaning process that one might imagine. In other words, comparing two coals, one with the other, each might have the same amount of refuse, the same amount of materials to be thrown away, but that is not any criterion of the washing difficulty.

If we eliminate the easy materials and consider just those at ten points difference or fifteen points difference in specific gravity, we are confining ourselves to the Rheo method of the coal cleaning proposition. I think that a great deal will develop from this start that Mr. Bird has made.

In reference to Mr. Morrow's paper there is one thing in connection with the Montclair No. 10 air cleaning plant that is a very significant thing, and that

is the matter of operation. The comparison of cleaning results from any given cleaning plant, be they wet or dry, should include the care and intelligence of operation.

It is a well-known fact among coal cleaning men that the cleaning results in the Birmingham district are very high grade. In spite of the fact that none of the recently introduced processes have found their way very forcibly into the Birmingham fields, nevertheless it would be a ridiculous thing for anyone to attempt to go to the Birmingham field and improve on the washing results they are now getting with plants that are ten, fifteen and twenty years old.

It would be a very difficult matter to go in with a new process, costing the same or costing twice as much, and guarantee any more yield or guarantee any lower ash or make any excellence guarantees whatever.

In connection with the Library plant, we were faced with one difficulty among others that I want to mention now. There have been in this field, owing to the fact that the dry cleaning process is more or less an infant—a strapping infant, perhaps, but nevertheless young in the field—competent plant operators and one of our principal difficulties is in finding them. In the Birmingham field where they have developed for nearly two generations now, there is usually someone in the field who can be called upon and who can intelligently operate a jig, but in the West Virginia field unfortunately there are a great many jig plants that are not being operated with the intelligence that they are in the Birmingham field.

I do not say that is a general situation, because I see one of my West Virginia friends up there who knows how to operate a jig. Nevertheless there is a great deal of difference between the training and the result to be obtained when the operators are trained, and when the same sort of equipment is operated more or less carelessly or ignorantly. That was the situation that Montclair had when we started. We had no air cleaning operators who had been trained, and it took some months to train one. The result was, the chemical results which you perhaps heard about in the early days at Montclair No. 10 plant, were not nearly so satisfactory as they are now, and I am wondering if Mr. Morrow would not be willing to give us some idea of how that plant is operating now. Anything that he is at liberty to give in result or late figures, I for one would appreciate.

CHAIRMAN NEALE: At times Mr. Arms referred to the plant as No. 10 and others as the Library, it is one and the same plant.

JAMES A. MORROW: I do not happen to have any actual figures with me, Mr. Arms. I will have to rely on my memory, but I would say that about eight months ago the ash and waste was running between 37 and 40; today it is running 64, and has been coming up in a continuous curve for the last six or seven months.

I notice that Mr. France seems to think a plant can be run without any trained help, but I do not think that will work out. I do not care what kind of a plant it is, wet or dry. You must have trained help and you cannot depend on common labor. A man must be interested in his job and have some idea what he is doing. I would say one of the main things is to give him the ac-

tual operating results for the previous day on the next morning when he goes on the job.

JAMES R. CAMPBELL: I wish to take this opportunity of saying that the exemplification just given by these two gentlemen, is in my judgment, a better performance than the exemplification of a dry table, given by Mr. Tait. In other words, I do not believe that any of us would consider that a reduction of 11 per cent ash to 8 per cent is very highly efficient or that a reduction of one point sulphur down to 1.7 per cent is highly efficient, in view of the fact that most of us know that the Pittsburgh coal is capable of a higher reduction in ash and sulphur, particularly in sulphur. I am not sure but that the dry plant referred to is giving a much higher reduction in sulphur, while probably not quite up to the maximum. The Pittsburgh coal will reduce in sulphur by modern and efficient methods, about 30 per cent, depending on the original sulphur content. The test referred to by Mr. Tait was apparently made on 4-inch x 0 inch with a small percentage of oversize coal, say up to 7 inches.

MR. MORROW: I would like to ask whether, on a commercial basis, anybody has ever handled with any class of apparatus 7 inch coal down to dust on one pass. I mean on a commercial basis and not a test.

CHAIRMAN NEALE: Can someone answer the question?

No one made any comments.

# COÖPERATIVE CONTROL OF COAL PURCHASES BY GAS WORKS

By P. E. RAASCHOU

*Professor in Applied Chemistry, Royal Technical College, Copenhagen*

Although it is of universal interest for the coal producing as well as the non-coal producing countries that every effort is made in attaining a rational utilization of coal for its many applications, and to endeavor to use for each special application the particular grade only which is best fitted. Those countries, which have to import all coal used, have a very special interest in the economical utilization and right application. This latter is naturally of vital importance to gas and coke works.

Large consumers who are in possession of well-equipped laboratories and who have at their disposal scientifically trained chemists can very easily maintain scientific coal control, whereas many medium sized and small consumers, whose total consumption does play a prominent part in the fuel economy of a country, in many cases have been unable to handle such a task by themselves.

These small consumers have more use for simple and practical specified methods, which can be performed without the assistance of scientifically trained minds and from which it is possible, in a comparatively short time, to obtain analytical results of sufficient accuracy, than for methods which give results with an accuracy of several decimals.

Furthermore, it is of the greatest importance to these consumers, in judging the quality of the coal available on the market, to get an opportunity for comparing their analytical results.

The problem has therefore been to work out simple analytical methods which could be standardized, and to organize coöperative utilization of the results gained.

I shall have the honor, briefly, to outline the present arrangement which the Danish Gas Works Association, members of which are mainly municipal works, have established and which for the last four years has been working to the fullest satisfaction of the members involved and therefore now is intended to be further developed.

There are about 112 gas works in Denmark, the majority of which supply towns with from about 6000 to 125,000 inhabitants with gas and coke; only coke is used for domestic purposes.

The coal which is on the market, comes from Great Britain, Poland, Germany and in special cases from the United States and they show a great difference in qualities.

The manner of proceeding is, briefly, that the gas works in following standardized method, takes out average samples from all coal deliveries and then tests these samples in accordance with the standardized methods made specifically for this purpose, which enabled them to make proximate analysis and to draw valuable conclusions about the quality of the coke which can be produced from the coal tested. The results of these analyses, as well as all information in regard to the shipment of the coal, such as the name and location of the mine from which the coal was shipped, the quantity shipped, the name of the gas work, the general condition of the coal as to the size, etc., all this information, etc., is forwarded to the Association which then without any delay prints all this data on special blanks. As soon as these blanks are filled out they are distributed to all the active members in the corporation, and in this way it is made possible for them to be familiar with all the valuable information regarding coal available on the market, and accordingly be governed in future purchase of coal.

From the ash and water content in coke, the calorific value can be calculated with good approximation, while a rough calorific value of the coal can be determined from the results of the approximate analysis by using the formula given by *Gontal*.

It would, of course, also be of great importance to be able to include a sulphur determination in this series. However, so far it has not been possible to simplify this determination to a point where it can be made quickly and safely by a person untrained in chemistry. All sulphur determination including volatile as well as total sulphur on coal from the various gas works are therefore made at a central laboratory.

It is the intention of the Association in the future also to have the determination of the fusing (softening) point of ash in oxidizing atmosphere, included in this series of testing, as this determination is very simple and easy to make.

The coöperative control has induced many gas works to use grades of coal which are much better adapted to the production of coke, as they previously used. While most of the works previously aimed at getting a coal which gave the largest amount of gas simultaneously with cokes which were barely useful, they are now paying considerable more attention to the quality of the coke and are trying to

buy coal which not only gives a large amount of gas, but at the same time produces a low ash coke of the very best quality. It has been proved that some miners have made a special effort by introducing improved methods for cleaning and sorting the coal at the mine, to satisfy the more rigorous demands now put up by the gas works.

This change in the viewpoint of the gas works, which has been the first practical result of the educational influence of this coöperative system, has in several cases been of great economical advantage, and it has forced the importers of coke to raise the quality of their coke in order to stay on the market. By using coal low in sulphur, several of these gas works now have been able to increase the capacity of their gas purifying installation, while in some cases extensions of these have been avoided.

In the following will be given a complete description of the simple method for making the proximate analysis and for determining the softening point of the ash as now adopted by the Danish Gas Works Association. The ash and water determination gives results which agree with those obtained by the ordinary method for making these analyses; the quantity of coke found is about  $1\frac{1}{2}$  per cent higher than when determined in a platinum crucible after *Muck's* method. All weighings are performed on a fairly inexpensive balance with a maximum sensitivity of 0.01 gram.

*No. 1. Volatile Matter.* Ten grams of finely pulverized coal from the average sample is weighed into a special iron crucible having a diameter of 52 mm. and a height of 35 mm. The crucible, with the lid on is placed on a crucible support as shown on Figure 1 and this support rests on a tripod 200 mm. high. A cylindrical iron chimney about 95 mm. high with a diameter of about 70 mm. and a thickness of 0.5 to 0.75 mm. is placed around the crucible (Fig. 2). This iron chimney has three small openings, both at the top and bottom, which fits around three projecting parts or fins on the crucible support, in order to prevent the chimney from tipping over too easily. Besides the three small openings mentioned above, this iron chimney has a large opening at the top, which during the determination of the volatile matter, is kept covered with a plate.

The crucible is heated with a Bunsen burner in such a way that the inner cone of the flame just touches the bottom of the crucible. The length of the flame should be about 180 to 200 mm. using about 300 liters of gas per hour. After 20 minutes ignition, the crucible is allowed to cool off and the cake of coke just formed is removed and

weighed. The size and density of the cake of coke gives quite a few indications as to the physical quality of the coke which can be produced from the coal tested.

*No. 2. Ash Determination.* This determination can be made either by transferring the cake of coke from the volatile matter to an

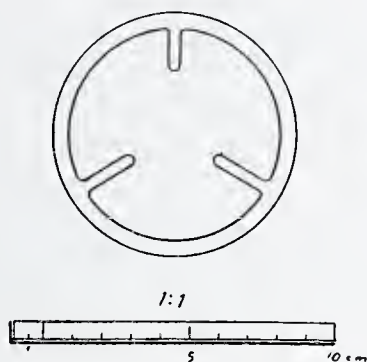


FIG. 1

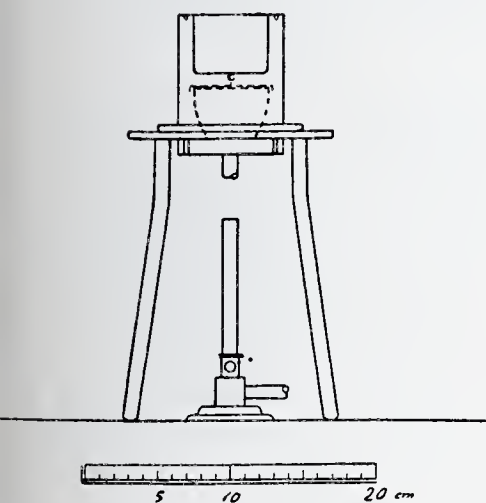


FIG. 2

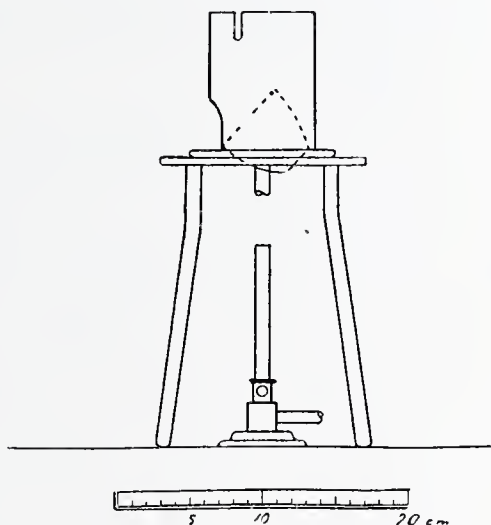


FIG. 3

ignited and weighed porcelain crucible or by weighing a new sample of 10 grams pulverized coal into the crucible. The porcelain crucible used is about 52 mm. in diameter and about 43 mm. high. The crucible is placed on the support in an inclined position and the iron chimney is placed on the support with the large opening at the bottom as shown on Figure 3. The ignition is repeated with occasional

stirring until constant weight has been attained, which usually takes about three hours.

*No. 3. Determination of Moisture.* Ten grams of the pulverized coal is weighed into a crucible and dried in a gas heated drying oven at a temperature of 105°C. until constant weight is attained.

The determination of the fusing point of ash in oxidizing atmosphere will be made in accordance with the following method:

*No. 4. Fusing point of ash.* The determination is made by comparing the softening temperatures of small cones made of the ash to be tested, with softening temperature of Seger cones with known fusing point.

In making up each cone, a mixture of 1 gram of finely pulverized coal ash and 0.1 gram dextrin is moistened with enough water to make a plastic mass. This mass is then formed into the shape of a Seger cone and dried at a temperature of 100° to 200°C., after which the cone is fairly hard and ready to use.

Two of the ash cones are now compared with a series of 6 Seger cones, for instance, No. 08A, 05A, 02A, 2A, 5A, and .8, corresponding to the following temperatures: 940°, 1,000°, 1,060°, 1,120°, 1,180°, 1,250°C.

All the cones are mounted on a refractory base which has been mixed and formed on a porcelain plate of black fireclay moistened with enough water to give it the proper plastic consistency. The porcelain plate with all the cones are then transferred to a Meker muffle furnace size No. 3D, which is heated with a blast burner. The heating must at first be done slowly, not only as a protection to the furnace, but also to insure the proper drying and heating of the fire clay and uniform temperature at all places or points in the muffle.

During the heating the appearance of the cones is watched through the inspection hole in the door of the muffle, and as soon as the first noticeable bending of the test cone has taken place, the heating is discontinued and the furnace is allowed to cool off.

After the cooling the porcelain plate with the cones is removed from the furnace and by comparing the condition of the test cones with the condition of the Seger cones, it is possible to determine a certain temperature interval inside which the fusing point of the ash is located.

If greater exactness is desired, the test can be repeated by using, for instance, 3 or 4 Seger cones, which all have fusing points lying inside the first determined temperature interval and by such repeated test it is possible to shorten the next temperature interval to about 20°C. inside which the fusing point of the ash is located.

Many a superintendent of gas works who previously was unable to get such analytical control as outlined above, is now regularly and with the greatest interest making use of these test methods, which have fully proved to give comparatively, results of the necessary practical exactness.

The establishing of such an arrangement as made by the Danish Gas Works Association has naturally opened up many possibilities for more extensive coöperation for solving the many, both technical and economical, problems which the gas works meet within their daily life, and a special result has been the arrangement of courses for the superintendents and their assistants by which they get a thoroughly scientific, up-to-date education in the science of fuel and its applications and also in the performance of the many important chemical and physical tests of products of importance within the gas industry.

THE REASONS FOR THE NEED OF CLEAN COAL  
FROM THE STANDPOINT OF THE POWER AND LIGHT INDUSTRIES

By F. R. WADLEIGH

*Consulting Fuels Engineer, Consolidated Gas Company, New York*

*Read by Thomas R. Alexander, Jr., Associate Professor of Chemical  
Engineering, Carnegie Institute of Technology*

In this address I shall state, in outline, the general reasons for the need—I shall make it stronger and say demand—on the part of the power and light industries for clean coal; not attempting to go into detailed figures or statistics showing the specific reasons for such demand, from the plant operation standpoint.

The power and light industries must have clean coal, regardless of type, rank, grade or size, if they are to operate their plants with the highest possible all-around efficiency and economy—that is the answer, in a few words, to the question implied in the title of this address.

“CLEAN COAL”

From the early days of the coal industry this has been a persistent topic of interest and argument to both producer and consumer. Probably every written contract for supplying coal has in it a clause calling for the shipment of coal “free from slate, bone and other impurities,” or words to that effect.

“All the slate they buy, is not merely a fraud upon their finances, but a tax upon time, in putting in and taking out so much waste materials from grates and furnaces.” This statement, quoted from the well-known report of Professor Walter R. Johnson, written in 1849, has reference to the purchase of coal and forms part of certain suggestions made as to the selection and buying of coal; it applies equally well to today’s coal purchases and proves that the value of clean coal was even then fully appreciated. Indeed sometime previous in 1849 the washing of coal was practiced in the Durham (England) field in order to obtain cleaner coal for making coke. The coal carbonization branch of the public utilities can show, therefore, an unbroken demand for clean coal, covering nearly a century.

Before discussing directly the interest of the public utilities in clean coal, I shall give some data showing the amount of coal consumed at public utility power plants and gas works.

As is well known, we have little accurate statistical information covering the whole country regarding the consumption of coal, either by classes of consumers or by localities.

As far as the Federal Government is concerned, the only accurate coal consumption figures it issues are first, those covering public utility power plants; second, the amount of coal used in coke manufacture; third, foreign bunker coal; fourth, coal used on steam locomotives by Class I railroads. Coal used in the manufactured gas industry is also given annually but usually the data is about three years old when published.

The United States Bureau of Mines also makes quarterly "trend of consumption" estimates, based on returns from a limited number of consumers in each leading group. These estimates are useful and probably not far out; they constitute the best service the Bureau can give, with the limited appropriations it has available.

Of the figures given in the following tables, consumption of coal at public utility power plants is reported monthly by the United States Geological Survey. Consumption of coal and coke by the manufactured gas industry was furnished by the American Gas Association, as made up from reports of its members.

*1. Total Consumption of Coal by Public Utility Power Plants in the United States*

	<i>net tons</i>
1928 (eight months).....	26,485,479
1927.....	41,888,497
1926.....	41,310,828
1925.....	40,222,006
1924.....	37,556,125
1923.....	38,954,338
1922.....	38,178,907
1921.....	31,585,284
1920.....	37,123,855

*2. Coal and Coke Used by Public Utilities in the Manufacture of Gas-Net Ton*

	<i>Anthracite</i>	<i>Bituminous</i>	<i>Coke</i>
1927.....	294,000	9,381,000	4,568,000
1926.....	601,000	8,941,000	4,227,000
1925.....	960,000	7,400,000	3,800,000
1924.....	1,308,000	6,580,000	3,754,000
1923.....	1,096,000	6,844,000	3,189,000
1922.....	1,098,000	6,588,000	3,387,000
1921.....	1,833,000	7,114,000	2,413,000
1920.....	1,953,000	7,778,000	2,025,000

Taking the figures given in the foregoing tables, it is estimated that the gas and electric utilities consume annually about 8.6 per cent of the entire coal production of the country, which was, in 1927, 597,859,000 net tons and about 10 per cent of the bituminous coal output of 517,763,000 net tons. Using annually such a large amount of coal, it can be readily understood that the utilities are much interested in its preparation, the methods used, and their efficiency, as directly affecting purchases and use results.

For, apart from the character and quality of the coal as it exists in the ground, the most important factor in determining its shipment condition after it has been brought down in the mine, is its preparation and the effectiveness with which the latter is carried out, particularly as regards the cleaning of the coal, the removal of the so-called "extraneous ash" or mineral matter, before shipment.

Preparation, therefore, is the especial element in coal production to which the public utilities give the greatest consideration because of the important part that it plays in the general results obtained from the use of coal.

#### GENERAL RESULTS OF THE PREPARATION OF COAL

The effective preparation of coal:

- (1) Makes possible the satisfactory use of low or medium grade coals by certain groups of consuming industries for purposes in which the use of such fuels would otherwise be difficult if not impossible.
- (2) Gives greater all-around efficiency in every use of coal.
- (3) Makes for conservation of our higher-grade coals.
- (4) Lowers handling and transportation costs.
- (5) Gives coal greater ability to compete with other fuels.
- (6) Ensures uniformity in quality of coals as shipped.

#### WHAT IS MEANT BY THE TERM "CLEAN COAL" AS UNDERSTOOD BY THE PUBLIC UTILITIES

In the common, everyday use of the term, it means coal as shipped from which there has been removed, either by hand or by mechanical means, as much as possible of the physical impurities, extraneous, non-combustible materials; usually mineral matter in some form associated with the coal as mined.

Professor Louis, in his recently published book, "The Preparation

of Coal for the Market," says, "Coal in common with practically all other mineral substances which man has learnt to extract from the crust of the earth, requires, as a rule, some form of preparation to fit it for utilization, in the best possible manner, in the various industries which human ingenuity has developed."

Now, the most important part of coal preparation consists in cleaning it and in removing the various other substances, incombustibles, minerals or rocks, or sedimentary deposits that are found in the coal bed or above or below it and which become mixed with the coal when it is mined or broken down at the working face. And, as the general results obtained from the use of coal, either in ovens and retorts or in boiler furnaces are, to a considerable extent, dependent upon the manner and effectiveness with which the coal has been cleaned before shipment, naturally the public utilities are much concerned in preparation results and should be also, as many of them are, interested as well in methods and their relative efficiencies.

Clean coal means to them greater economy, higher efficiencies, wider range of capacity in plant operation and also in the retort and oven, higher yields of better coke, gas and by-products. And this regardless of the kind or grade of coal, whether semi-bituminous steam or coking, high volatile gas or lignite or anthracite; whether used in stokers, in pulverized form, in ovens or retorts and regardless of the size of coal.

Complaint is frequently made by the consumer, public utilities and others as well, that many coal producers do not properly clean their coal. Such complaints are frequently well founded but there is another side to the question—the economic side. To clean coal properly costs something, for equipment, supervision and labor; it adds to the total mine operation costs. While it is true that every coal producer should clean his output as far as may be possible; as a matter of practical business ethics, he is in duty bound to his company to seek some compensation for the additional expense incurred. And the consumer, public utility or other, should be willing and ready to foster the clean coal movement by paying a fair price for a clean product and by making some distinction as to comparative prices, differentiating between the producer who cleans his coal efficiently and the one who does not.

Another angle of the price question comes in here. Granted that the public utilities are willing to pay more for cleaner coal, can they

collect revenue sufficient to enable them to pay a higher price for clean coal? Or, will the presumably greater efficiency and economy in plant operation with clean coal make up for its higher cost? And here also enters the matter of uniformity in coal quality. Will the clean coal be kept uniformly so over the contract period? That is a question of much importance to the public utility consumer. The every-day use of a coal that is consistently uniform in character and quality means in power plant, gas and coke works, a more economic operation and, in the case of the two latter, high average yields and high grade products as well. If such results follow from the use of uniform quality well-prepared coal, then the public utility of whatever class, should be and generally will be, willing to pay for what he gets—a fair price for a good article.

On the other hand, the greater demand, steady business with satisfied customers, sure to follow the shipment of coal of unvarying quality, means steadier, more uniform mine operation, which will make up for some at least of the cost to the mine operator of shipping clean coal.

#### EFFECT OF ASH REDUCTION ON ASH SOFTENING TEMPERATURES

There is another phase of the "clean coal" subject, which is of great significance to the public utilities. I refer to the effect of ash reduction on its fusing or softening temperature, its clinkering tendency. As has been pointed out by Messrs. Sinnott and Wood, "Excessive purification may produce coal yielding ash, the melting point of which is relatively low, and thus reduce the value of the purified coal for certain industrial purposes."

It is needless to say that the gas and electric utilities are vitally interested in this phase of coal cleaning, as to both coal used under boilers and that used in gas retorts, generators and coke ovens.

We are still, however, in the experimental stage of ash-softening determination and their exact relation to the clinkering of coal in actual use. And as to the effect of cleaning coal in different degrees, on its ash-softening temperature, there is but little experimental data available, although research work now being carried on, especially that by the United States Bureau of Mines, will undoubtedly add considerably to our knowledge of the whole subject. The fact that the public utilities are assisting the Bureau of Mines in this particular investigation is sufficient evidence of their interest in the subject.

As Dr. Lessing has pointed out, the cleaning of coal is not a small matter or easily accomplished. It has many ramifications which cannot be thoroughly understood without considerable study and thought; not only must the amount of ash be known, but also its character, structure, distribution and effects on the use of the coal with which it is associated.

The growing realization of the importance of the whole subject of coal preparation is strikingly shown by the great increase during the last five years in the amount of research work devoted to it, in the use of new methods and in the number of papers and addresses on the subject that have been published. For instance, the "Engineering Index" for 1927 lists some 60 papers or addresses devoted to coal preparation and in the first seven months of this year over 40 have been published or delivered.

Knowing the importance of coal preparation in its effects on their use of coal, the public utilities are now giving close attention to the whole subject; to the character of the coal ash; to the methods and equipment used for its reduction; their efficiency, capacity and the results they give in reducing the ash and sulphur content of the coal—thus raising its heating value and yield possibilities—the two primary objects of coal cleaning, whether the coal is used for producing electrical energy or gas, or coke and by-products.

In past years, the public utilities have usually been content to purchase coal on its general character, reputation and cost and with due regard to the results obtained in actual use, without much, if any, investigation of mining or the preparation methods used and their efficiency.

Today, however, the utilities are not satisfied with such meager information regarding the coals they use but are finding out and studying how the coal they purchase is mined and prepared, the kind of equipment used and what results should be obtained from its use. In other words, the public utilities are today paying greater attention than ever before to the subject of clean coal, whatever its rank, grade or character and whatever use they may make of it.

And it will be to their own advantage, if those interested in the production and sale of coal for the public utilities would understand that the situation is as described and that, if they desire to increase the use of coal by the utilities and keep out competing fuels, they must give closer attention to the preparation of their product and see that, as shipped, it is clean or, at least, as free from extraneous

matter as the use of efficient methods and unceasing attention can make it. They (the producer and seller of coal) must realize that to secure and keep public utility contracts, they must not only have the necessary tonnage of coal of the character required, but that it must also be shipped at all times in the cleanest possible condition.

Apart from results obtained in its use there is another strong reason for the interest of the public utilities in clean coal; namely, the losses they incur by paying transportation charges and handling costs on material that has no value as fuel.

For instance, our railroads hauled in 1926, 7,417,000 cars of bituminous coal, with an average load per car of 52.7 tons. Assuming that the coal averaged 10 per cent ash, each car contained 5.27 tons of ash. If, by cleaning the coal, the ash content has been reduced to 8 per cent (a quite possible result), the freight bills of the consumers would have been reduced by the amount paid on 8,162,000 tons or, assuming an average freight charge per ton of \$2.50, \$20,405,000. The railroads would, of course, lose that amount of revenue, but we are not concerned with that side of the matter, and they will in turn likewise benefit in their use of coal.

Dr. Lessing has also given an illustration and estimate of the losses due to ash in coal, using British production figures and conditions.

He estimates, assuming a yearly production of 250 million tons and 10 per cent average ash in the coal, an average rail haul of 43 miles and freight rate of about 3s, 8d, per ton (about 90 cents) that 4,500,000 pounds Sterling (or about \$21,800,000) are spent on hauling useless material. Adding other losses due to handling and disposal of ash and lower combustion and carbonization efficiencies, Dr. Lessing adds "The country's non-productive expenditure on this score, (total losses from ash) may, therefore, be put at the stupendous figure of from \$10,000,000 to \$20,000,000, a waste which surely would be a worthy subject of the closest scientific, technical and economic examination."

If we take the coal tonnage consumed by the public utility power plants alone in 1927 (41,888,500 tons) and assume its average ash content to have been 10 per cent (a reasonable assumption) the public utilities concerned paid freight on 4,188,885 tons of incombustible material. If better preparation had reduced the ash to 8 per cent, the amount of incombustible would have been 3,351,080

tons, which, at \$2.50 per ton average rail freight cost, would have shown a saving to the utilities of \$2,094,437, in that one item of fuel cost, not to mention probably an equal or perhaps greater amount saved in handling and use.

The public utilities are advocates of clean coal from another standpoint, which, while not directly affecting their operation, is a matter that concerns both the utilities themselves and their customers. I refer to the part clean coal plays in the general abatement of waste, which, as one of our greatest engineers and economists has said, is a total asset and has no liabilities.

The cleaning of coal is true service on the part of the producer. It makes his product easier to sell and his business more profitable; while to the utility using it, it affords greater combustion and carbonization efficiency, hence lower unit output costs, more profitable operation and better service to the public and to the owner.

"The better we serve, the more we earn."

# THE SAND FLOTATION PROCESS

By T. M. CHANCE

*Philadelphia, Pennsylvania*

The sand flotation process is a float-and-sink method of separating materials of different specific gravities, the light material floating in the upper portion of the separating medium and the heavy material sinking therein. It is based upon the fact that any relatively finely comminuted insoluble solid (such as sand) if maintained suspended in a liquid by continuous agitation, will form a mixture that will possess physical properties similar to those of a fluid of relatively high specific gravity. This mixture we term a "fluid mass" and such fluid masses may be thought of as mechanically maintained liquids obeying most of the laws of hydrostatics.

## OPERATION OF THE PROCESS

In commercial practice a cylindro-conical container for the fluid mass is generally used, this design providing an effective method of withdrawing the refuse from the high density fluid mass. The lower part of such fluid mass is supported on an upwardly rising column of hydraulic water required for agitation, distribution of the hydraulic water being assisted by a slowly revolving agitator in the fluid mass. The coal is discharged by permitting a portion of the fluid mass to overflow and portions of the fluid mass admixed with the coal are removed by screening, such desanding being materially assisted by a comparatively clear body of liquid overlying the fluid mass in the container. The refuse is removed from the base through the rising current of hydraulic water, a waterseal being maintained by means of interlocked slide valves.

The above briefly outlines the basic elements of sand flotation. In practice further adjunctive devices are necessary such as means for removing very fine coal from either the feed or the fluid mass, settling tanks, sand handling systems, etc.

The sand flotation process may be used on coals varying from any size mined down to fine coal approximating the size of the sand used for the fluid mass. Treating large lump coal is simply a matter of designing devices to handle it. A sand flotation fluid mass will float a one ton lump as readily as a particle weighing but 1 gram.

The sand used is generally sized silica sand, the greater portion of which passes a 30 mesh and is retained on an 80 mesh screen.

### HISTORY OF DEVELOPMENT

The process was invented, and was experimentally carried out at Ocean City, N. J., in the late summer of 1915, by agitating a mixture of seashore sand and water, and introducing coal into the agitated mixture. The coal floated at the top of the mixture while the slate sunk through the mixture to the bottom of the container.

General research work was commenced in 1915 and has been continued up to the present time including the building of working models of many different types. Such research has been essential to determine the elemental physical constants of the fluid masses used in this new method.

Owing to the industrial disturbances following the termination of the war, the first commercial plant was not built until 1921. This consisted of a separating cone 7 feet 9 inches in diameter of the same general character and type as those now used. This cone was installed at the West Nanticoke breaker of the Grand Tunnel Coal Company by Mr. H. O. Staples, was at once successful in cleaning coal for market and is still in daily use preparing the output of the mine. A few years ago two cones 4 feet in diameter were added to this plant and used for cleaning the smaller sizes of coal. The plant as so equipped has shown a capacity to prepare and ship 20,000 tons a month or about 900 tons per day of 8 hours.

During 1922 and 1923, three cones 15 feet in diameter were installed and during subsequent years cones 13 feet 6 inches, and 12 feet in diameter respectively were installed at a number of plants. There are now 28 plants in the anthracite regions equipped with this process and comprising cones of the dimensions given in Table I.

### ANTHRACITE OPERATING RESULTS

These plants have an estimated capacity to ship more than 12,000,000 tons of 2,240 pounds per year.

The experience gained in the construction and operation of these anthracite plants is useful in designing and operating plants cleaning bituminous coal.

The plant at West Nanticoke on several occasions has been used for running tests upon a commercial scale, (several hundred tons)

TABLE I  
SAND FLOTATION PLANTS

DIAMETER	NUMBER OF CONES	LOCATION	OWNER
4'-0"	2†	West Nanticoke	Grand Tunnel Coal Company
7'-9"	1†	West Nanticoke	Grand Tunnel Coal Company
7'-9"	2‡	Port Carbon	South Penn Collieries Company
7'-9"	2	Avondale	Geo. F. Lee Coal Company
7'-9"	2	Olyphant	Hudson Coal Company
12'-0"	2	Mt. Carmel	Shamokin Collieries Company
12'-0"	2	Shamokin	Stevens-Chapin Coal Company
12'-0"	1‡	Port Carbon	South Penn Collieries Company
12'-0"	1	Plymouth	Kingston Coal Company
13'-6"	4	Natalie	Madeira, Hill & Company
13'-6"	3	St. Clair	St. Clair Coal Company
13'-6"	2	Newcastle	Repplier Coal Company
13'-6"	2	Excelsior	Northumberland Mining Company
13'-6"	4	Scranton	South Penn Collieries Company
13'-6"	2*	Jeddo	Jeddo-Highland Coal Company
15'-0"	1	Beaver Brook	Chas. M. Dodson & Company
15'-0"	1	Winton	Rose Coal Company
15'-0"	1	Lafin	Hudson Coal Company
15'-0"	1	Minersville	Pine Hill Coal Company
15'-0"	1	Dixon City	Glen Alden Coal Company
15'-0"	1	Harleigh	Harleigh Coal Company
15'-0"	1	Nanticoke	Nanticoke Valley Coal Company
15'-0"	1	Junedale	Coleraine Collieries Company
15'-0"	1	Moosic	Old Line Coal Company
15'-0"	1	Winton	Winton Coal Company
15'-0"	1	Wilkes-Barre	John Ames Coal Company
15'-0"	1*	Avoca	Suffolk Coal Company
15'-0"	1	Avoca	Clifford Coal Company
15'-0"	4*	Marvine	Hudson Coal Company
15'-0"	1	Duffy's Field	Hudson Coal Company
Total....	50		

\* Now being installed.

† Same breaker.

‡ Same breaker.

on anthracite coals, and in making such tests has been operated at specific gravities of from 1.60 up to about 1.78. Higher gravities have been obtained by mixing with the silica sand commonly used a small percentage of trap rock sand or of magnetic iron ore tailings, having specific gravities of from 3.0 up to 3.30, as compared with about 2.65 as the average specific gravity of the silica sand or quartz sand ordinarily used.

In current practice in cleaning anthracite coal the specific gravity most commonly used is between 1.70 and 1.75, but gravities above 1.75 may be used occasionally in cleaning coals the specific gravity of which is slightly above the average specific gravity.

Throughout the anthracite regions visual inspection of both the cleaned coal and the rejected refuse is used to determine the efficiency of the separation, but float-and-sink tests with solutions of zinc chloride are rapidly displacing this older method of inspection both at sand flotation breakers and those of the older types.

Operators of sand flotation plants using float-and-sink tests to determine the percentage of slate and of high ash bone in the cleaned coal, and the percentage of coal and low ash bone in the rejected refuse, find that if properly operated the process substantially reproduces those indicated by float-and-sink tests made upon the uncleaned (raw coal) feed.

We believe that operators using the process have generally found that they can ship to market coal of higher grade than they formerly produced, thus enabling them readily to meet market requirements.

#### BITUMINOUS DEVELOPMENT

Sand flotation was applied to the washing of bituminous coal in October 1925, at the tipple of the East Broad Top Railroad and Coal Company at Mt. Union, Pennsylvania. The general design of the units installed follows anthracite practice and the operation of the plant only varies from such practice in practically producing dry fine coal and in the lower densities required for bituminous cleaning.

Two cones each 10 feet in diameter were installed which have developed a shipping capacity of approximately 4,500 tons in 8 hours. The coal from  $4\frac{1}{2}$  inch to 1 inch is treated for the domestic trade in one cone at a density high enough to produce the desired grade. The coal below 1 inch is screened, the undersize passing  $\frac{3}{8}$  inch being by-passed dry and the 1 inch by  $\frac{3}{8}$  inch washed at a density appropriate to the steam and metallurgic fuel requirements of this size.



However, the margin of profit in bituminous mining is not always sufficient to justify large expenditures for the additional plant necessary for extensive draining or drying equipment, or for installing other methods of handling the fine coal and the monetary return from cleaning such fines must be certain if the increased capital and operative costs are to be repaid.

The Mt. Union plant is operated at from 1.4 to 1.5 specific gravity depending upon the character of the coal to be treated. The sand used is the same as at anthracite installations. A 300 gallon per minute makeup water pump is provided and from 200 to 300 gallons of fresh makeup water are added per minute to compensate for water losses. No water reclamation unit is used, and would not be desirable because the waste of this makeup water prevents excessive accumulations of sludge in the circulating water.

### RESEARCH

In closing it would seem appropriate to acknowledge the assistance in furthering many necessary investigations that has been given us by those using the process.

Small sand flotation test units have been installed by Lehigh University, the Universities of Illinois, Washington and British Columbia, and a laboratory cell is now being built by the University at Leeds in England.

Research thus made possible at these educational institutions may develop much that will be useful to those using the process.

## THE CHOICE OF A COAL CLEANING PLANT

By GODFREY M. S. TAIT

*Consulting Engineer, Washington*

Not many years ago, coal "preparation" was at most mines confined to the hand picking of slate, if indeed any "preparation" was considered necessary. Now, however, due to an excess of coal supply, the operator is experiencing such acute competition that it behooves him to produce the very best fuel that is possible from his coal, and naturally this can best be accomplished by thorough cleaning to reduce the ash, and where possible, the sulphur content.

With an infinite variety of marketable coals in our various producing fields, it follows that many, and in some respects quite dissimilar apparatus and processes should have been developed to meet local conditions. The coal operator, therefore, finds himself faced with the problem of adopting that form of process or apparatus which will most completely adapt itself to the coal he has to treat, the local conditions at his mine, and the needs of the consumers to whom he expects to dispose of his product.

The first step in solving the problem is of course to submit his coal to a careful, accurate, sink-and-float test to determine what is the theoretical limit to which the ash content can be reduced, and from this data to construct a "washability curve." With this data before him he can then proceed to select the process and apparatus that can most closely approach the theoretical ash reduction when applied to his local conditions. For example, the decision of his choice between "wet washing" and "dry washing" may be determined in some instances by the availability of a suitable water supply, and conditions enabling the satisfactory disposal of his wash-water and sludge.

Also, in some instances, he may be planning to only clean certain sizes of his product, which will again influence him in his decision as to the nature of the proposed process.

"The proof of the pudding is the eating" is an old and apt phrase, and therefore there is much information to be gained by considering what has already been done in the way of practical operation of coal cleaning plants on a commercial scale, and hence the following information on plants now in actual operation is instructive.

## FLOTATION PROCESS

*Draper washer.* This wet process is very popular in Wales, South Africa, France and Spain where it is doing good work.

The apparatus which is of extremely simple nature comprises a cast-iron housing of vertical pipe, the coal being fed downwards through a smaller centrally located pipe, where it encounters an upward current of water, the action being that the lighter coal particles are carried up and out with the overflow water, while the heavier slates and impurities sink to the lower part of the apparatus, where they are withdrawn through a suitable valve. This process is especially fitted to treat fines or slack, though coal up to nut size is

TABLE I

Amount of coal treated.....	100 tons
Make-up water.....	2 tons
Average wash in coal.....	14 per cent

## RESULTS OBTAINED

SIZE OF COAL	CLEAN COAL	ASH	TONS REFUSE
	<i>tons</i>	<i>per cent</i>	
1½- to ¾-inch.....	28.50	5	1.5
¾- to ⅜-inch.....	15.12	5.5	0.88
⅜ to 0 inch.....	39.14	6.8	2.86
Dirt.....	7.47	83	7.47
Filterings (used in plant).....	3.60	28	1.40
Total.....	86.36		14.11

sometimes handled. Table I is a record from a plant 100 tons per hour.

This plant comprised three units, as under this process it is of course necessary to have a separate unit for each size, and even then extreme accuracy of the proportion of water flow to coal feed is essential to avoid impurities carrying over with the coal or vice versa.

The Chance sand flotation process, in very successful use in this country, is an improvement on this process, sand being added to the water to control its specific gravity, thus enabling the use of larger units of modified design and avoiding the necessity of sizing the coal before washing.

## LAUNDER SYSTEM

The launder system as its name implies accomplishes the separation of the heavy ash from the coal by passing the material treated through long troughs, or launders, where the action of the water allows the settlement of the heavier impurities, and the carrying over of the lighter or coal particles in the water stream. Perhaps the best example of this system, and one that is meeting with great success in this country, as well as abroad, is the Rheolaveur System. In this process the launders are used in connection with "Rheo" boxes which draw off the product at various stages of the launders—a very distinct improvement. This process also is adapted to the re-treatment of the middlings, and the process will handle un-screened coal.

TABLE II

	MAIN FEED 100 PER CENT			WASHED COAL			REFUSE		
	Ash	Float	Sink	Ash	Float	Sink	Ash	Float	Sink
	<i>per cent</i>			<i>per cent</i>			<i>per cent</i>		
Egg.....	18.81	89.0	11.0	6.5	100.00	0.0	75.5	1.21	98.79
Stove.....	17.70	88.0	12.0	6.5	99.75	0.25	84.2	1.42	98.58
Nut.....	15.65	90.0	10.0	7.6	99.31	0.69	80.2	0.52	99.48
Pea.....	14.40	91.0	9.0	7.2	98.69	1.31	80.6	3.09	96.91
Buckwheat.....	14.40	92.5	7.5	10.4	96.76	3.24	82.8	2.79	97.21
Rice.....	13.70	93.0	7.0	10.1	96.36	3.64	81.9	3.40	94.60
Barley.....	15.90	90.0	10.0	12.9	93.64	6.36	61.4	21.50	78.50
Composite.....	16.12	90.0	10.0	7.68	98.78	1.22	80.2	1.76	98.24

The figures in Table II are taken from published results by the Glen Alden (anthracite) Coal Company, treating 4- to 0-inch un-screened coal.

## TABLE SYSTEM

For want of a better designation the next type of washer may be referred to as the table type of washer, as this class of coal washer owes its inception to the well-known Wilfley table used for the concentration of copper and other ores.

The first of these tables known to the writer was the Massco Table, which appeared about 1906. Then came the Butchart, the Diester, and others, all of which, however, retain the basic principle

of a deck supplied with riffles, over which a mixture of water and coal is fed, the table being oscillated or "jigged" to assist in the separation of the heavy from the light particles treated.

With this class of table the various sizes of coals are treated on separate tables, several units of which are included in the average plant.

The efficiency of this class of table is comparable with the figures already submitted, varying, of course, with the nature of the coal treated and its particular ash.

#### ADDITIONAL SPECIALIZED TYPES

Other specialized types of washers have also been developed for treating specific sizes or grades of coal, for example, the Hydrotator process as employed at the Middle Creek Colliery of the Philadelphia & Reading Coal and Iron Company. This process employs large shallow circular tanks supplied with water-driven mechanical stirring or agitating devices, the coal being fed in a downward direction to the center of the tank where it is allowed to settle against an upward current of water, the gentle agitation of the stirring devices resulting in a slow but very complete separation of the impurities from the fine coal.

#### "DRY WASHING"

The great success met with by the various wet washing processes naturally created a demand for some method that could produce similar results in those localities where water was not available, and from this demand there developed still another type of coal cleaning process, sometimes referred to as "dry-washing."

The origin of this idea is said to have grown out of experiments that had been conducted with what might be termed a dry-type Wilfley table, in which the water supply was replaced by a blast of air blown up *through* the table through perforations between the riffles of the deck. This table although it was designed and used to separate fertile from infertile seeds, wormy beans from whole beans, etc., pointed the way to the possibilities of air-separating coal, and at the present time there are at least two types of tables on the market successfully employing air for coal separation.

Such a plant is in operation at the Montour No. 10 Mine of the Pittsburgh Coal Company where eight sizes of coal from 2½-inch

down to  $\frac{1}{16}$ -inch are handled on eight "Arms Air Cleaning Tables." In this type of plant a separate table is required for each size of coal handled, but very efficient results are claimed.

In the Peale-Davis System the principle of the old Wilfley table is still further departed from, the riffles on the deck being replaced by partitions whose function is quite different from the cascading classification formerly employed. This table has the advantage that all sizes of coal can be handled on the same table simultaneously

TABLE III

PEALE-DAVIS TABLES—PENNSYLVANIA MINING MACHINERY CORPORATION.  
CLEANED COAL RESULTS—TESTING PLANT, ST. BENEDICT, PA.,  
MINIMUM OF 150 TONS PER TEST

SEAM	DISTRICT	SIZE	ASH	SULPHUR	RECOVERY	THEORETICAL ASH (LOWEST ASH POS- SIBLE TO OBTAIN AT RECOVERY SHOWN)	ACTUAL RESULTS			
							Cleaned coal		Refuse	
							Ash	Sulphur	Ash	Sulphur
		<i>inches</i>				<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
(1) Pitts- burgh	Pitts- burgh	7 x 0*	11.2	1.9	94.5	7.5	7.9	1.7	61.0	5.0
(2) Pitts- burgh	Pitts- burgh	4 x 0	10.8	2.2	94.4	6.0	6.2	1.8	61.2	6.2
(3) "B"	Cambria County	3 x 0	7.48	1.86	96.5	5.50	5.76	1.17	55.32	19.55
(4) Alabama		4 x 0	18.6		88.0	10.95	11.4		68.0	

*Note:* The average of the above four tests are within 0.33 of 1 per cent of theoretical perfection as shown by the washability curves at the given recoveries.

\* Some of this coal and refuse up to 10 inches but not much over 7 inches.

without previous separation, the writer having seen slate up to ten inch pieces handled without difficulty, while at the same time the separation of the fines was all that could be desired; also these tables are in use in capacities up to 300 tons per unit with retreatment facilities for handling 50 tons per hour of "middlings." The extreme flexibility of this process leaves the percentage of ash removal under complete control.

With a raw coal containing 10.50 per cent ash (Miller Seam, Penna.) that it was theoretically possible to clean down to 7 per cent ash;

actual operation showed 7.5 per cent ash content in the cleaned coal, the table operating at 250 to 300 tons per hour. The theoretical refuse having an ash content of 45 per cent at a 91.50 per cent recovery against an actual ash content of 42.50 per cent on leaving the retreatment table. The data in Table III show performance with this table on various coals.

From the many actual installations, a few of which have been touched upon, it will be seen that coal cleaning has now reached a state of perfection where any cleaning problem can be handled, provided that sufficiently intelligent information is available as to the local conditions, the nature of the coal to be treated, and the market for which it is intended.

The author desires to lay great stress on the necessity that the coal producer or operator know exactly to what uses his washed coal is to be put before deciding on a cleaning plant. For example, to go to the expense of cleaning a coal, unless assured of some market preference to be obtained thereby, is on the face of it a waste of money. Likewise to install a washery that will produce a product suitable, and in fact, to be preferred by your customers, is absolutely essential. For example, your customers may insist on a very low moisture content in the washed slack in which case air washing would have special advantages.

Then again, the nature of the ash to be removed is worthy of a great deal of thought. If it is of a non-fusible nature, it may not be objectionable in even comparatively high percentages, whereas if the fusing point is low, it may pay to go to the expense of removing every possible fraction of a per cent.

For example, if you have a large production of slack or fines, which are a drug on the market, and can only be sold for the bottom dollar, it certainly will not pay to add the cost of a washery to handle them, when a washery designed for the larger prepared sizes may suffice. On the other hand, if washing your slack and lowering its sulphur content, and reducing its ash, will admit its use in a profitable market from which it has hitherto been excluded, calling for a higher grade article (such for example as coke making or pulverized fuel furnaces), you will be justified probably in making a very considerable outlay for a plant that will produce this very much desired result.

Then again, no matter what type of plant is contemplated, the prudent coal operator should compile a business forecast in which a

reasonable estimate should be worked out as to the dollars and cents gain to be expected over *the life of the plant* due to its use, so that he may be in position to write off his investment on a conservative and accurate basis. With this before him he will be assisted in deciding as to the type of plant he can reasonably afford to purchase and the number of units that he is justified in installing.

The first step to be taken before going into the qualifications of the various processes should be a careful canvass of existing and possible markets for washed coal. Next should be considered the particular characteristics of the coal to be treated to determine to what degree each prepared size can be improved by such treatment. Consideration should be carefully given to the present design of the existing plant to ascertain its adaptability to the addition of washing equipment, and what form of equipment can most readily be installed in the local premises within minimum structural changes. Then comes the question of first cost, and not less important operating expenses, which figures should be compared with the margin of gain to be expected from selling your quality of washed coal on your market.

Such consideration of the elements entering into the choice of a washer will in most cases indicate clearly what type of plant to purchase, how large an investment is justifiable, and give a reasonably accurate picture of the total benefits to be derived, which benefits in the majority of cases will be found to be very considerable.

#### DISCUSSION

MR. H. L. OLIN (University of Iowa, Iowa City, Iowa): May I ask a question that is very vital and important in the Middle West where the bituminous industry is seasonal and where mines are in operation mainly in the winter time, concerning the practicability of wet washing due to the freezing of the finished product after being loaded?

I find marked opposition to even a reasonable discussion of the question among Iowa consumers due to the fact that the cars come to the plant in such a condition that they have to be unloaded with crowbars. I should like to ask Mr. Tait whether in his opinion such conditions would rule out wet washing should it be advisable to attempt washing at all.

MR. TAIT: The water content in the shipped coal, of course, has to be kept as low as possible in such a territory. Some of the information today indicates that some of the wet wash coal, for example the Chance, has a very low moisture content, but it stands to reason, of course, that a dry washed coal would stand a better chance of remaining dry than one that has been wet before shipment. As a matter of fact the slack coal that is air washed is very hard to wet.

MR. CHANCE: May I answer that question because I find that the low moisture results reported from the Mt. Union plant have at times been questioned by those not familiar with the reasons that permit the shipping of coal of the moisture content reported.

Chapman and Marks, the English investigators, have recorded a number of experiments on the use of centrifugal drying devices for removing moisture from very fine coal and I think that others who have carried out either laboratory or large commercial experiments on fine coals passing a millimeter have secured like results, namely that on coals of such fineness the surface tension effect is so great that sufficient centrifugal stress cannot be developed to tear the moisture film from the coal particles. Therefore but little increased drying effect can be secured (with centrifugal speeds that are ordinarily possible) over natural drainage due to gravity. The principal function of the centrifugal is to greatly accelerate the time of drainage, as a force much greater than that of gravity alone is available.

However, this force is never sufficiently great to actually disrupt the film of water held to the coal dust particle by the forces of surface tension. Therefore, theoretically there should be but little difference in the ultimate drainage effect possible if a sufficient area and time is provided with ordinary type of gravity drainage screens. (The shaking screens now in use for this purpose tending to more rapidly clear the meshes of the water removed than can occur with the older forms of gravity screens.) This effect of course is far greater in the case of the centrifugal drier.

From the above premises it would appear that if the extremely fine coal is once wetted then thermal means (either by direct heating, by the use of relative humidity processes, or by low pressure evaporation) must be employed for driving off the moisture.

Where the physical characteristics of the coal will permit the practice, we believe that this problem is best met by not wetting the fine coal and by so cleaning the coarser sizes washed as to reduce the ash sufficiently to permit the fines to be by-passed in their raw state. Even under these conditions we frequently find that the fine coal itself will contain from 8 to 10 per cent moisture as dumped from the mine car. For a number of years Alabama coals have been treated in this way, the coal passing a  $\frac{1}{2}$ -inch or  $\frac{3}{16}$ -inch mesh being by-passed raw and the coarser coal washed.

However the results reported from these Alabama washeries do not indicate that they have found it possible by this method to ship a 1-inch washed slack coal running but 4.5 to 5 per cent moisture as is the practice at Mt. Union. The reason for the difference we believe to be due to degradation because if any degradation occurs in the washing process, the fine coal so produced will remain of high moisture content and therefore the prescreening of the fines only lessens the moisture problem. On the other hand with the sand flotation plant at Mt. Union the degradation is negligible and if a 1-inch by  $\frac{1}{4}$ -inch coal is sent to the washing unit practically a 1-inch by  $\frac{1}{4}$ -inch coal is discharged therefrom with but a negligible amount of fine coal due to degradation. This granular material is readily dewatered on the desanding screens and therefore the total moisture of the mixture of such dewatered coal and raw fine coal is easily held within the limits noted.

That this method of overcoming the moisture problem has been successful is indicated by the fact that during the three years this plant has been in operation I do not know of a single car of slack coal being condemned at the point of unloading due to freezing in shipment—the best evidence of low moisture in the shipped product.

In many cases it is quite easy<sup>2</sup> to follow this procedure with coals that have comparatively impure fines, because with the sand flotation process it is possible to drop the density to such a point that only the very pure coarser coal will float, crushing the bony material so discharged and rewashing it. The resultant yield for a given ash content may then approximate that which would obtain if all the coal, including the fines, were washed at a higher density, with the important difference that the latter procedure would mean a relatively wet shipped product as opposed to the drier material produced by this by-passing operation.

CHAIRMAN ASHLEY: There is one phase that possibly was not brought out; i.e., that when west of Indiana and in Indiana your coals have from 13 to 15 per cent moisture naturally.

JAMES S. DRINKWATER (Engineer, Link Belt Company, Chicago, Ill.): Mr. Tait in his opening remarks, mentioned the Draper washer as being the popular one in Great Britain.

Their first plant was put in at Llwynpia, and, I believe, is still running. Two plants were put in at the Crown Fuel Company, Cardiff, and Port Talbot. Two and one-half years after installation these had not been put into actual regular operation. The next plant was put in for Guest Keen & Nettlefold at Cwmbran. After about eighteen months of intensive effort to make this plant a success it was ripped out.

I think if numbers count for anything the Simon-Carves plant is the popular plant in Great Britain, and it is only right for the audience to know that Simon-Carves have put 160 plants in actual operation, and not one has been rejected or turned down in any way.

MR. TAIT: I said, "one of the popular plants." No doubt there are many more popular ones which I have not had a chance to get in contact with. The only reason for my rising is to remove any idea that it was the only popular plant in Great Britain. I think 160 plants speak for themselves. Simon Cartage has built 95 per cent of those erected in Great Britain.

MR. H. S. RICHARDSON (Vice-President, West Kentucky Coal Company, Paducah, Ky.): I would like to ask some of the speakers whether they have any general figures as to the approximate cost of installation of various sizes of cleaning plants based on the number of tons per hour capacity of the plant. I think that would be of interest to all of us who are contemplating plants of this character, who have to figure with the dollar and cents feature.

I think many things are technically and physically possible that are not commercially feasible, and if some of you gentlemen are in the sales department, as I happen to be, and are also interested in the operating department,

from the standpoint of preparing your product to meet the increasingly difficult demands of purchasing agents, I am quite sure you agree that the dollars and cents part of it is relatively important.

Supposing I want to put in a plant of 100 tons per hour capacity, is there any reasonable range of cost to estimate for that plant, or may the cost range be very wide depending on local conditions.

MR. CHANCE: Are you talking about part of the plant or the whole arrangement?

MR. RICHARDSON: I would like an estimate of all the additional equipment that you would consider necessary in addition to the normal existing equipment of a well equipped mine operating today.

MR. CHANCE: A complete one hundred ton per hour plant equipment will cost from \$25,000 to \$35,000. The Mt. Union plant has shipped approximately 4500 tons in eight hours. The cost of reproducing that tippie, including all of the transfer arrangements, concrete dam for fresh water, and lump coal handling equipment etc. would be from \$125,000 to \$150,000, depending on the location and layout. The washing capacity of the plant is approximately 400 tons an hour, and it has demonstrated a shipping capacity of 600 tons an hour.

CHAS. ENZIAN: We are just completing installing a second dry cleaning plant, and the cost, including the handling of the coal through the plant, dumping mine rock and loading the cleaned coal onto railroad cars is \$1,013 per ton. It is a 400 tons per hour capacity plant.

## ECONOMIC PHASES OF THE FERTILIZER INDUSTRY

By C. H. MACDOWELL

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With your indulgence, I shall attempt to deal with the broad, fundamental economic and scientific facts underlying the fertilizer industry, rather than with the more restricted facts and figures relating to the immediate situation. In order to do this, some knowledge is necessary of the development of soil science and the consequent growth of the fertilizer industry.

Man has observed from the early dawn of history that certain soils are more fertile than others; that certain substances such as dung and animal matter increase plant growth. "Sow you golden corn," says Virgil, "in land where grew the bean, the slender vetch or the fragile stalks of the bitter lupin." Legumes fixed air nitrogen millenia before the building of Merseburg.

However, it was not until the last years of the eighteenth and the first half of the nineteenth century that the study of the soil became preeminently a science instead of an art. The world is deeply indebted to Sir Humphry Davy, to Boissingault, Lavoisier, Liebig, Lawes, Gilbert, and other members of that great "fifth estate" of science. At the time Liebig was carrying on his researches, bones were already a commodity in international trade. Liebig roundly declared "England is robbing all other countries of their fertility. Already in her eagerness for bones she has turned up the battlefields of Leipsic and Waterloo and of the Crimea; already from the catacombs of Sicily she has carried away the skeletons of many successive generations. Like a vampire she hangs upon the neck of Europe—nay, of the whole world—and sucks the heart blood from nations without a thought of justice toward them, without a shadow of lasting advantage to herself." Evidently bones were a highly competitive article.

The inception of the commercial fertilizer industry really dates from the time that Liebig in Germany advocated the acidulation of these bones, and Lawes in England in 1842 patented his process and started to manufacture superphosphate from bone in order to make the phosphate more readily available as plant food. Poudrette was being produced in France. Peruvian guano and Chilean nitrate of soda had already been imported into Europe, but Lawes' venture was

the first definite chemical manufacturing operation for the preparation of fertilizer. Mineral phosphate gradually replaced bone as a raw material, and the discovery of phosphate rock in the United States in the period from 1860 to 1890 practically completely eliminated bones for the preparation of superphosphate. The demand for this product had grown to such an extent that the world supply of bones would have been entirely inadequate even for bloodthirsty England.

With the rise of industry in Europe, the drift to the towns and the pressure of increasing population, the demand for food became more and more urgent. Food was being imported from overseas. Although the newer agricultural methods were slowly and reluctantly adopted, the average acre yields of western Europe were more than doubled in a little over two generations. Fertilizers had much to do with this increase, and they became an integral part of the agricultural economy.

When the world needs something badly it secures it. Research disclosed what was needed in the way of plant food raw materials and reagents and they were located, transported and utilized. Sulphur bearing ores assumed additional value, and smelting operations through sulphur fume utilization as sulphuric acid could be carried on extensively in settled sections. The packing industry found a market for much of its offal through fertilizer channels, as did oil seed pressing ventures. Industrial and city waste such as leather scrap, hair and felt, sugar waters, garbage and sewage, became of value. Health and sanitation were protected and materials of farm origin of no further value to the town were returned to the land to increase production. Sodium and potassium nitrate, Peruvian guano, bones, phosphate rock, became important commercial commodities. For a long time potash was in short supply, but the discovery of practically inexhaustible deposits in Germany and available to cheap water transport relieved the world of worry on that score. Phosphorus bearing materials were being located in various parts of the world. The steel industry was producing as a sub-product basic slag, a phosphorus carrier. Looking far ahead, nitrogen was the disturbing short supply element. Soil science was also making progress, and more knowledge was constantly being accumulated as to plants' ways and means. Biological chemistry explained many mysteries. All these additions to agricultural knowledge have been of great value, and could be of far greater value if more fully utilized by farmers.

The ultimate destination of plant food should be the area within the root growth reach of the plant. Ample plant food must be taken to the plant in the right forms and in proper proportions, one element to the other, if the work to be done by the plant is to be best carried on. The element carriers work together. Ample balanced rations are as necessary for the proper and profitable development of plants as they are for the live stock of the farm. The task of the fertilizer maker is to assemble, prepare and deliver the farmers' proper needs in plant foods with diligence, with despatch, and at reasonable prices.

In Europe the general method of distribution has been for each factor to ship his particular material directly to the farmer who applied the ingredients separately or mixed them together in varying proportions as he saw fit. Transportation distances are short; tracts under cultivation are comparatively small, labor plentiful and cheap, agriculture intensive. Factory assembled complete fertilizers are rarely used. Fertilizers are mostly broadcasted.

In America, while ingredients are applied separately or home mixed, the larger part of the tonnage is shipped in the form of mixed fertilizers of varying ratios. Farm labor is scarce and expensive. Application is almost entirely by mechanical distributors in hill and drill, making for enriched local areas. The preferred placement seems to be under the crop bed, putting part as near the seed as it can safely be placed without retarding germination. Soil solutions move up and down, with a more decided upward tendency than downward and with practically no lateral movement except under unusual flood conditions. Phosphoric acid has little soil penetrating power and surface applications are rather ineffective. The same is true to a less extent of potash. Inorganic nitrogen compounds move more freely through the soil, the size of soil particles, surface tension and water conditions determining the rate of movement and possible leaching; coarse soil particles permit a freer movement and larger losses. The old type organic nitrogen compounds have little mobility. The proper placement of fertilizer is of extreme importance, and perhaps the weakest link in plant feeding is properly designed agricultural implements. Much remains to be done in this direction.

Tests made in this country seem to indicate the hill or drill method produces greater yields on the applied crop than does broadcasting. Applying fertilizer in complete form places the interacting elements in the same vertical zone. Separate applications are apt to place the nitrogen here, the phosphorus there, the potassium somewhere else—a more haphazard method.

The use of complete mixtures is increasing in England. German manufacturers are manufacturing quite concentrated complete goods extensively, and pushing their use. If properly carried out, the complete factory mixture would seem the better where the three elements are to be applied and where materials assembling and distribution can be economically carried on.

The American trend in plant construction has been toward moderately large units located in the center of large consuming districts, quickly serving nearby needs, and away from very large plants, even though the latter if run to capacity might have slightly lower f.o.b. car costs. These integrated smaller plants have relatively the same fixed capital relation to output cost as have the larger plants. Incoming freights at these strategically situated units are on concentrated high analysis materials such as sulphur, phosphate rock, high grade potash salts, nitrate of soda, sulphate of ammonia and even anhydrous ammonia. Outgoing freights on finished products are all within the one to three dollar area. At many of these local plants sulphuric acid and 18 to 20 per cent superphosphate are manufactured in addition to the complete mixed goods. This is a highly efficient and economical process. In the manufacture of the acid 97 to 98 per cent of the sulphur is recovered as sulphuric acid, and in the acidulation of the phosphate rock well over 95 per cent of the phosphorus is rendered available as plant food. This superphosphate is unquestionably the cheapest source of available phosphate laid down on the farm, if made near point of use. As long as this is true, superphosphate will maintain its place in the fertilizer industry.

One of the chief economic factors involved in this system is the choice of the cheapest assembling points for necessary raw materials with due regard to incoming freights and cost of power and supplies, consistent with nearness to point of consumption, so that demand may be quickly supplied at the smallest out-freight cost. Fertilizers are distributed to farmers within a very short period, particularly in the United States. Farmers generally make late decisions as to needs and kinds, and are influenced by weather, by markets, and by their purchasing power. In some sections, supply merchants who finance farmers' operations control the type of fertilizer the farmer uses.

Since 1920 American fertilizer demand has fluctuated rather violently with farm purchasing power, and cheaper price per ton rather than cheaper cost of plant food has often been in demand by dealer and farmer. This has necessitated the use of a large tonnage of

so-called "filler"—an expensive and unnecessary addition to the cost of plant food on the farm. Its use is utterly indefensible from a scientific or economic standpoint. Its use has prevented the farmer lowering his production costs to the extent he might have lowered them if he had used mixtures of higher concentrations.

Ville of France in the 1860's compounded and successfully used for cereal and vegetable production a formula consisting of 7 per cent ammonia, 6 per cent available phosphoric acid and 7 per cent potash—a total of 20 per cent plant food. If all the complete fertilizers and fertilizer ingredients consumed in the United States were mixed together, the average analysis would be not far from 3 per cent ammonia, 10 per cent phosphoric acid and 3 per cent potash—a total of 16 per cent plant food;—a lower analysis than Ville used in 1860. Fertilizers with materially higher plant food content than this average can and should be produced with the present day high grade, low cost fertilizer materials. The use of filler is inefficient and uneconomic, and should be eliminated to as great an extent as possible.

Agricultural authorities are stressing the economics of higher grade mixtures and are also endeavoring to reduce the number of grades offered. Standardization along this line will effect important manufacturing economies.

There has been much discussion of late concerning very highly concentrated fertilizer combinations, and the economics of them have been stressed. There is nothing especially new in the idea of greater concentration. Certain of these products have been on the market for years and a limited tonnage has been distributed, more particularly to high freight overseas destinations. Generally speaking these materials have cost more to produce at plants, and unless out freights were high there has been no advantage in their purchase. Triple superphosphate containing 45 to 48 per cent available phosphate has been made in Belgium for years, yet the Belgian farmer has used little of it. Potassium nitrate was used as a fertilizer seventy-five years ago. Basic patents on the preparation of ammonium phosphate expire this year; this article has been on the market for years.

It is only since synthetic ammonia manufacture has assumed such large proportions, and other than the usual channels of distribution have had to be found, that the making of especially concentrated mixtures has appeared really practical. Such highly concentrated compounds are now being made in a large way in Germany, and a vigorous, effective effort is back of their distribution. As they are

founded primarily on nitrogen fixation, this element bulks large in their ratios. Germany also has potash at low freight assembling cost. Phosphorus suitable for chemical or thermal treatment is the element which must be purchased from abroad. The German offerings contain lower phosphorus ratios to nitrogen and potassium than present practice requires in America. France, with coal for nitrogen fixation, with potash, and with phosphates which can be delivered at low cost from nationally owned phosphate rock mines in north Africa, possesses national assembling advantages for the manufacture of concentrated fertilizers. The United States has large phosphate rock reserves at the coast and in the interior, has coal and a growing nitrogen fixation industry, interior by-product ammonia which can if necessary be produced and shipped as anhydrous in tank cars rather than as sulphate of ammonia, and finally has domestic potash production in California and can obtain European potash at low water freights at all ports. Well located potash deposits would strengthen the American situation.

For economical production these concentrated products must be made in a large way at centralized plants. In the United States they will have to meet the competition of mixtures having somewhat lower total plant food content, but made most efficiently and economically in local plants serving their neighborhoods and meeting the definite requirements of soil and crop. The present system permits of much greater flexibility in formulation. Appreciably higher total plant food values per ton can be produced with present high grade fertilizer raw materials than is now usually the case, and very quick and efficient service can be given to the local farmer.

The great refinement of the highly concentrated fertilizer salts may somewhat limit their plant food value. The incidental impurities in less highly refined products, such as lime, sulphur, manganese, magnesia, iron and iodine, are of importance in plant nutrition. The method of using such concentrated materials on the farm is still in an experimental stage. In the United States, with our vast territory and inland rail distribution, the economic problem involved in the production and distribution of concentrated fertilizers is not so simple. The preparation of these materials is a distinct advance in the art. However, at present the greater development of nitrogen fixation and greater accessibility to other raw materials, as well as greater use of water transportation for assembling and shipping make the economic conditions in Europe very favorable for their production. Here the

existing local plants meet the needs of agriculture and adequately serve the farmer during the short periods each year when he absolutely must have his fertilizer, and they can continue to serve by making appreciably higher concentrations with their present materials. When these extremely concentrated fertilizers, made at central plants, are able to meet the conditions of distribution and cost, they will become an important factor in the American fertilizer situation.

Nitrogen is the most expensive of the plant foods. Its cost has been materially reduced in recent years. It is the advertising element in the fertilizer group—it makes for size, something one can see. Let us digress a little and consider how this nitrogen is affected in the soil.

Sir John Russell in his splendid book "The Fertility of the Soil" explains with great clarity this subject. When plant residues, farm-yard manure or other organic materials are added to the soil they do not serve as the actual food of plants, but only as the raw materials from which the food is made. The true food is the nitrate to which the organic matter gives rise. In most cases plants absorb their nitrogen in the form of nitrates exclusively. Owing to the losses in nitrate caused by drainage, there is rarely any great stock of it in the soil—frequently not enough for a season's growth. In the soil, organic matter slowly undergoes decay. The nitrogenous portion may be converted partly to ammonia, partly to nitrogen gas which is lost. No specific micro-organism seems to be responsible for this decay. Enzymes, earth worms, fungi and bacteria may all take part in the decomposition. The ammonia so produced, however, is rapidly and practically completely converted by specific bacterial action to nitrates. It has been demonstrated that the process takes place in two stages: the ammonia is first converted into nitrites by one organism, and the nitrite then changed to nitrate by another organism. Sir John Russell summarizes the process thus: "We have, then, three reactions going on: nitrogenous plant residues change to ammonia, ammonia changes to nitrite, nitrite changes to nitrate. Of these the last is the quickest, the second is slower and the first is slowest. The first change, therefore, limits the rate at which nitrates are produced: if we could speed up this change we should hasten the other."

The fertilizer manufacturer recognizes this condition, and has met it by using less of the organic materials to furnish nitrogen in his mixtures, and more of the inorganic ammonium salts and nitrates.

Manure and plant residues will always play an important part in agriculture, but more as a bacterial media and as a corrective for the physical condition of the soil than as the source of plant foods. Certain organic nitrogenous by-products of industrial and city wastes, most of which come originally from the farm and properly should be returned to the land, will continue to be used in fertilizers near points of production. Better utilization of many of these products, however, is now being made in stock feeds. New sewage products, as dried activated sludge, have distinct agricultural value and naturally will be consumed within their economic range. The utilization of sewage in this way makes for sanitation.

In the United States the traditional method of farming, except in certain areas given over to vegetable and fruit culture, is the use of extensive planting as opposed to intensive yields. Phosphorus is generally the first element supplied. Then comes potassium, and then nitrogen. In cereal culture in the central basin, legumes and crop residues are largely depended on for nitrogen maintenance. The experiment stations advise this. In any system of agriculture legumes, manure, and crop residues must play an important economic part as a means of adding and conserving nitrogen in the soil. Complete cereal fertilizer ratios are relatively low in nitrogen. One  $N_2$ , six  $P_2O_5$ , one  $K_2O$ , has been a popular ratio in the central west, but the trend is now toward a 1-3-1 or a 1-3-2 ratio. It will be some years, however, before the nitrogen demand for corn growing becomes important in the United States, although there is need for more purchased nitrogen at this very moment, even in the black soil corn belt. Nitrogen fertilization grows apace, but the progression is steady and not sudden. Consumption is steadily increasing, and will continue to increase gradually with the growth in population and improved farm economy; but the economic factors are mostly lacking here which make for a rapid and violent increase in the use of nitrogen in other parts of the world, where population pressure and restricted acreage induce most intensive cultivation. There is a promising field for increased nitrogen consumption in the United States in fruit orchards and for pasture land fertilization.

Ammonia from by-product coking plants plays a leading rôle in the American fertilizer industry, and will continue to be a basic economic factor in the nitrogen situation. By-product plants are located in various fertilizer consuming sections of the country, and ship their ammonia as sulphate of ammonia to the fertilizer works. The day is not far distant, however, when by-product and synthetic nitrogen

plants will ship part at least of their ammonia to fertilizer manufacturers as anhydrous ammonia instead of as sulphate of ammonia. Anhydrous ammonia, with its more than 80 per cent of nitrogen content, can be carried far in tank cars at a low freight per unit of plant food.

In Europe the production of synthetic ammonia is already being linked up with by-product plants. Coke oven gas is being used as a source of hydrogen. Such a development may eventually follow in this country at points where the gas cannot be disposed of more economically. In Europe, also, gypsum is to a great extent supplanting sulphuric acid as a means of converting synthetic ammonia to sulphate of ammonia. It is interesting to note that Liebig, in his lectures on agriculture written in the first half of the nineteenth century, mentioned such a method of fixing ammonia. It was not, however, until the advent of synthetic ammonia that this method became an economic and practical necessity in Europe. In the United States the likelihood of the use of this procedure on a large scale is rather remote. Here cheap sulphuric acid is available. In fact, at times in the fertilizer industry proper there is a real problem in the disposal of acid. This has been occasioned by the fact that ore smelters have sought an outlet for their by-product acid in the fertilizer industry. Sudden large increases in production of by-product acid increase the difficulty of balancing production of superphosphate with demand, and have caused large over-production in certain sections of the country.

Farm economy and fertilizer economy are indissolubly linked; one reflects the other. Traditional methods of farming and national agricultural policies affect both alike. In east Prussia, with only twenty inches of rainfall annually on the average, bountiful crops are produced by intensive methods, mainly because of the judicious use of large quantities of fertilizer. The materials used are mainly soluble inorganic salts. The effects are rapid; the bacteria of the soil do not have to act initially on refractory organic matter before the nitrogen becomes available. Moisture is the sine quo non of successful agriculture, but even in regions where the supply of it is comparatively low, crop yields may be increased and improved by the wise and proper use of fertilizer. Growing time is shortened, maturity hastened, and resistance to drought and disease increased. The hazards of agriculture are decreased.

In this country, however, quality should be of even more importance in our farm economy than larger yields per acre. Nubbins on

the farm are economically ruinous. Time and money are squandered on the raising, harvesting and shipment of inferior products. This fundamental lesson must be learned by every American farmer before he becomes economically independent. It is essentially the rôle then of fertilizers in American farm practice not only to increase the yield per acre and hence decrease the cost of growing, but also to improve the quality and hence the intrinsic economic value of the crop. To these ends is the industry dedicated.

The development of nitrogen fixation in Germany by the Badische Co. on an enormous scale during the war and the subsequent use of the nitrogen for making fertilizer materials and finished fertilizers has introduced a new economic problem into the agricultural and fertilizer world. The present capital charge on these plants compared with the cost of new plants, and rapid improvements in the art resulting in larger yields—these factors must give the Germans low costs. Germany's nitrogen is a product entirely of German origin, except the bags in which it is shipped. It gives a maximum national return when shipped abroad. Germany needs export trade, particularly of this type. Hence her aggressive search for new foreign market outlets, for new types of product, and for new uses on special crops.

Other German industries in coal and potash have also become active producers of nitrogen and of finished fertilizers. All these interests are organizing or enlarging their sales promotion staffs, and are aggressively introducing their products in world trade. They are becoming very active in the United States. Other countries also are endeavoring to establish a nitrogen fixation industry, and world production is increasing rapidly. From a total production of 1,339,000 metric tons of nitrogen in 1927, competent authorities have estimated the 1931 world output will be approximately 2,332,000 metric tons—an increase of a million tons.

How much of this increased production coming in so short a time can be used profitably without seriously upsetting world agriculture? Where can it be used to best advantage? It represents an increased crop production of seven hundred thirty million bushels of wheat. The total 1927 wheat crop of the United States was eight hundred seventy-two million bushels.

In the upbuilding and maintenance of an efficient civilization fertilizers play a most important part. The social and economic consequences of their use are manifold.

# BY-PRODUCT NITROGEN AND THE FERTILIZER INDUSTRY

By CHARLES J. BRAND

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Up to 1914 the production of by-product ammonium sulphate in the United States played only a relatively small part in the fertilizer industry of the country. Its total production in terms of nitrogen in that year was 37,700 tons, representing an output of 183,000 net tons of ammonium sulphate. Of this output probably not more than 50 per cent was used in commercial plant food.

On the other hand, in 1914 we imported less than 650,000 tons of Chilean nitrate of soda, of which about 410,000 tons, representing 64,206 tons of nitrogen, were used as fertilizer.

How profoundly the situation has changed in the intervening years is shown by the fact that if 1913 be taken as 100 in the production of sulphate of ammonia, 1928 represents a production of 400. The production in the United States in 1928 will exceed 782,000 tons, with a nitrogen content of more than 160,000 net tons. Of this quantity roughly 65 per cent is used in the manufacture of complete fertilizer. This means that the farmers of the United States are spending between \$30,000,000 and \$35,000,000 a year for the ammonium sulphate in their artificial plant food.

## THE FARMER'S POSITION AND PROBLEMS

The farmers of the United States and of the world are confronted with a highly complex series of problems. Their economic situation could be greatly improved by the use of fertilizer. Many factors play a part in their use or non-use of fertilizing material. Undoubtedly the most important factor lies in their purchasing power, by which I mean, of course, the rate at which they are able to convert the products of their labor into goods and services furnished by other industries or other kinds of business. But this is not the only factor, important as it is. The farmer frequently overlooks the advantage he may gain from two of the factors involved in the use of commercial plant food: (1) the fact that a dollar invested on the average returns three in value of product; and (2) the fact that the quality of the

crops produced with adequate feeding is generally better than it would be without such treatment. A third factor of great importance is the farmer's knowledge or lack of knowledge of the advantages he may obtain, for upon his insight into the laws that govern crop metabolism and soil fertility depends largely the financial rewards he may attain from the use of artificial plant nutrients.

The farmer is the creature of the economic winds, storms and calms of the world quite as much as of the physical weather and climate that surround his operations. He must know much of the biological sciences and their subdivisions, such as plant physiology, plant breeding, plant diseases, plant and animal genetics, and animal nutrition and diseases, as well as agricultural chemistry in its application to soils, and crops and animal husbandry in the broadest aspects. In addition to this, he is required to know something of marketing processes, the interaction of economic forces, the repercussions of credit and finance upon his operations, and many other types of information such as are demanded in other businesses only of high executives.

#### RELATIONS OF AGRICULTURE TO THE COAL INDUSTRY

*Prima facie*, a coal conference may seem an unusual place to discuss agriculture and the fertilizer industry. However, the interdependence of the two is very patent and each should give thought to its reliance on the other. It occurs to me to mention only one type of problem common to both. This is the impossibility, or the relative impossibility, of regulating competition through control of production. It is frequently said that there are 23,000 coal mines potentially and 7500 actually operable in the United States. There are about 6,250,000 farms. In a specific sense millions of farms may be in more or less direct competition with one another. Every one of the two and a quarter million cotton farmers of the United States is in competition with every other. The same is true of the more than 2,000,000 wheat growers. Although the number of the units in the coal industry is far less than those in agriculture as a whole or those in specific farming industries, it is likely that the ultimate economic effects of the competition of its 23,000 units is perhaps much the same as the effects of the competition of the millions of units of agriculture.

In this respect the fertilizer industry is not profoundly different either from agriculture or from the coal industry. In the fertilizer industry there are over 600 independent, competing units, large and

small. Their efficiency in upsetting economic conditions seems to be fully as great as if their number were multiplied by 10, 50 or 100. Contrast this situation with such an industry as automobile manufacture, in which four enterprises do nearly 80 per cent of the business, and 30 do nearly 100 per cent.

The interdependence between agriculture and the coal industry is in many respects very real. A busy steel industry, coking large quantities of coal, and industrial centers consuming gas for fuel and light are of distinct interest to the farmer. They not only represent an activity of great potency in the production of plant food in the

TABLE I  
PRODUCTION OF BY-PRODUCT AMMONIUM SULPHATE, 1913-1928

YEAR	AMMONIUM SULPHATE	NITROGEN CONTENT	PER CENT OF 1913 RATE
	<i>net tons</i>	<i>net tons</i>	
1913	195,000	40,200	100
1914	183,000	37,700	94
1915	250,049	51,500	123
1916	288,265	59,400	148
1917	325,670	67,000	166
1918	379,278	78,100	194
1919	403,223	83,000	206
1920	499,463	102,900	256
1921	358,500	73,800	183
1922	476,761	98,200	244
1923	603,363	124,300	309
1924	569,622	117,300	292
1925	633,649	130,500	325
1926	690,967	142,300	353
1927	717,460	147,800	367
1928	(est.) 782,100	161,100	400

form of sulphate of ammonia, but they betoken an active industrial market for agricultural products. Similarly, a prosperous agriculture, consuming directly and indirectly huge amounts of industrial products and energy, is a powerful factor in the well-being of many if not most urban industries.

Within a relatively short period sulphate of ammonia has become the largest source of nitrogen in chemical plant foods. So true is this that it is now the key product in the determination of the prices of nitrogen in the world market. It may not be amiss to remind you that nitrogen, phosphoric acid and potash are the most essential

materials in crop nutrition. Other less common elements, such as manganese, magnesium, iodine, sulphur and copper, play a varying part, but the three first mentioned are the outstanding factors in crop nutrition.

In 1913 approximately 55 per cent of the world's nitrogen was supplied from nitrate of soda. Ten years later only about 32 per cent was obtained from that source, and its importance—despite the fine character of the material—has continued to diminish. In the meantime, sulphate of ammonia, cyanamid, calcium nitrate and the synthetic products of various catalytic processes have assumed a major rôle in the world supply.

### THE TREND OF AMMONIUM SULPHATE PRODUCTION

I am indebted to Mr. C. J. Ramsburg, Vice-President of The Koppers Company, for the figures showing the production of ammonium sulphate in the United States given in Table I. They show not only the quantity produced annually in a rising curve, but the nitrogen content and the percentage of increase over the production in 1913 which is taken as 100 per cent.

The rate of increase shown will probably not continue. Our steel industry has perhaps reached its greatest expansion, and its growth henceforth will be much more gradual. There are still many beehive ovens that can be converted into by-product ovens. With the growth in the use of smokeless fuel that we may reasonably expect, it seems likely that more coal will be coked in the future than in the past, but we may safely assume that in the fifteen-year period between 1928 and 1943 we shall not witness an expansion of 400 per cent in the production of by-product ammonium sulphate. The operation of competitive forces will likewise tend to repress expansion, as the market must absorb not only a determined production of Chilean nitrate of soda but all the synthetic nitrogen products as well as the by-product sulphate of ammonia.

### PRICES OF AMMONIUM SULPHATE COMPARED WITH PRE-WAR PRICE AND WITH PRICES OF OTHER MATERIALS

The average price of sulphate of ammonia in New York during the year 1913 as reported by the Bureau of Labor Statistics, was \$3.14 per 100 pounds. The price of this carrier of nitrogen, in common with that of other carriers, reached hitherto unknown heights during

the war, the average for 1918 being \$6.70 per 100 pounds.<sup>1</sup> Thereafter prices began to recede, first very sharply in 1919, and then more gradually, until the prevailing New York price is now about \$2.35 per 100 pounds.

When we remember that the present index of all commodities is 150, or 50 per cent above pre-war, we can see why the farmer can afford to use sulphate of ammonia rather than most of the other commodities included in the all-commodity index.

Recently the Bureau of Labor Statistics has converted its index numbers to a 1926 basis. If 1926 is taken as 100, the index number of the prevailing price of sulphate is about 92. Comparing the pre-war price of \$3.14 with the present price, around \$2.35, sulphate of ammonia is about 25 per cent cheaper than it was before the war.

### PRICES OF AGRICULTURAL PRODUCTS

It may be of interest to examine briefly the prices of agricultural products in view of the foregoing statements concerning sulphate of ammonia, for the farmer must convert his products into money and his money into fertilizer in order to obtain the benefit of applying artificial plant food.

Despite the disadvantages under which the farmer has labored as shown by a comparison of the prices of his products with the prices of all commodities, he has been at a genuine advantage when the prices of farm products are compared with the prices of sulphate of ammonia and of the complete fertilizers in which sulphate of ammonia is used almost to the exclusion of any other material.

During the year 1927 the average price paid by farmers for the commodities usually purchased by them was 54 per cent above the five-year pre-war average. In other words, the index number was 154. During the months from June to September of 1928, the latest months for which figures are available, the index number of commodities bought by the farmer stood at 157. This number includes his purchases of fertilizer.

<sup>1</sup> The 1918 price quoted is that obtained for price index purposes by the Bureau of Labor Statistics through its regular reporting channels. The Barrett Company which is the largest distributor of sulphate of ammonia in the United States reports through its agricultural department that the average price received by it for sulphate of ammonia during 1918 was \$4.93 though in that year sulphate did go as high as \$8.00.

On the other hand, taking the 30 groups of farm products that represent by far the major part of the agricultural income of the United States, the index number for 1927 stood at 131; whereas for the four months June, July, August and September, 1928, it averaged approximately 143. This figure may be compared with sulphate of ammonia, the index for which was 92.

The cotton crop is the chief beneficiary of commercial fertilizers. During the elapsed months of 1928 cotton and cottonseed, taken together, have shown an average index number of about 150. It may be noted that the average price of all the individual fertilizer materials, combined into one index number, if 1926 is taken as 100, stood during the month of October at approximately 94.

#### PRICES OF COMPLETE FERTILIZERS

The composite price of mixed fertilizers per ton, based upon the 14 analyses or grades most widely used in the fertilizer-consuming sections of the United States, was 97.5 per cent of the 1926 base of 100. Comparison with the 1913 base is no longer possible since the Bureau of Labor Statistics changed its basing period. However, on a fair conversion the price of complete fertilizer is now about 9 per cent above the pre-war level; farm products stand about 41 per cent above, and commodities used by the farmer stand 57 points above.

#### THE ACHIEVEMENTS OF PRIVATE ENTERPRISE IN THE NITROGEN FIELD

We have given above a fair indication of what the by-product ammonia industry has done to supply our national need of nitrogen. Results in the synthetic field were delayed by a combination of factors, including the uncertainty whether the government itself might not be injected into the competitive production of fixed nitrogen at Muscle Shoals.

In 1920 we produced only 200 tons of fixed nitrogen. In 1927 the production had risen to 27,000 tons. In addition the cyanamid plant at Niagara Falls, Canada, the product of which comes largely to the United States, had greatly increased its output. This month a new synthetic plant at Hopewell, Virginia, has broken in its first 30,000 ton unit. Two additional units of equal annual capacity are nearing completion. This means that we have within the continental United States a productive capacity of approximately 60,000 tons of pure nitrogen by synthetic methods and that a productive capac-

ity of another 60,000 tons will be added during the next 18 months. It is estimated that by 1930 our production of synthetics, expressed as nitrogen, will be between 130,000 and 150,000 tons, or three times the maximum production that was planned at Muscle Shoals.

The increase of the production of nitrogen in Europe is one of the marvels of modern industrialism. Prior to the European war its production was negligible. At the end of the war a producing capacity of around 400,000 metric tons of nitrogen had been attained. Since that time increase in the efficiency of the older plants and the construction of new plants has added a producing capacity of no less than 700,000 metric tons, and it is estimated by Mr. F. C. O. Speyer, of the British nitrogen enterprises known as Nitram, Limited, that by 1931 the world's productive capacity of synthetic and by-product nitrogen will have risen from approximately 1,200,000 tons, the present output, to 1,900,000 tons.

What this enormous increase means can be visualized by the simple statement that the average annual increase in the consumption of nitrogen as such in commercial plant foods for the five years preceding 1914 was about 50,000 metric tons; while the average increase in consumption for the five years most recently elapsed has been about 75,000 tons.

These figures show the world increase, not the increase in the United States. The total consumption in the United States of nitrogen from all artificial sources in 1913 was 209,000 tons; in 1926 it was 310,000 tons.

#### A PROPOSED SOLUTION OF THE MUSCLE SHOALS PROBLEM

The facts and figures presented show the fallacy of undertaking government competition with private industry in the production of nitrogen at Muscle Shoals. At its recent annual convention in Atlanta, the fertilizer industry adopted a resolution calling for a solution of the problem of utilizing the government-owned plants at that place. A proper solution of this problem is of such distinct interest to producers of by-product nitrogen that I feel warranted in presenting here the resolutions adopted at Atlanta in detail for your information and consideration. In this connection you should remember that the average income from the sale of power over the last two years from Wilson Dam and the steam power plant has been \$1,300,000.

WHEREAS, the National Defense Act of 1916 decrees that the government properties at Muscle Shoals shall be devoted to the production of nitrates or other materials needed for munitions of war and useful in the manufacture of fertilizers *and other useful products*.

AND WHEREAS, the same act decrees also that the plant or plants provided for should be constructed and operated solely by the government and not in conjunction with any industry or enterprise carried on by private capital;

AND WHEREAS, under the existing temporary arrangements for the production and disposal of power, which are being handled as efficiently as circumstances permit by the War Department, electric power worth approximately \$1,300,000 has been sold annually during the last two years—an income which could gradually be increased if contracts for the sale of power for longer periods could be executed with assurance that their fulfillment would not be prevented by legislation or otherwise, except in the event of war;

AND WHEREAS, nitrates can now be produced more economically by other processes than the cyanamid process, and by the use of coal at less cost than by the use of hydroelectric power;

AND WHEREAS, the national defense act does not authorize the manufacture of phosphoric acid nor the purchase of fertilizer ingredients, nor the making of complete fertilizers, but the production of nitrates useful both in fertilizers and in other useful products;

AND WHEREAS, intensive investigations by the War Department have shown that, owing to changes and advances in the art of fixation of air nitrogen, the nitrate plants of this project are of little value for national defense;

AND WHEREAS, the area near Muscle Shoals and areas in contiguous states now have an insufficient supply of power or, with the development of industry soon will have, and plants for producing phosphoric acid and complete fertilizer in excess of the present demand are already in existence.

*Be It Hereby Resolved*, that The National Fertilizer Association, in convention assembled, petitions the Congress to authorize the sale, separately or jointly, of the Wilson Dam with its hydroelectric plant and the Steam Power Plant No. 2, safeguarding properly the public interest in navigation, flood control, and the development of the water-power resources of the Tennessee River; and in the event that this recommendation is not acceptable or can not be worked out, that these plants be leased by the War Department to be operated under the supervision of the Federal Power Commission with the coöperation of such state commissions as may have a direct interest in their operating, and that if neither sale nor leasing is found feasible the government shall continue to operate the plants through the office of the Chief of Engineers, War Department, selling the surplus power produced at the switchboard to the highest responsible bidder, giving such preference as may be fair and just to power companies operating in the Muscle Shoals area, but under regulations to be prescribed by the Federal Power Commission; that if the plants are sold or leased proper provision be made for their recapture in event of national necessity, and, if leasing is resorted to, that a suitable block of power be reserved for the use of the United States Department of Agriculture for the purposes hereinafter described.

*Be It Further Resolved*, that The National Fertilizer Association hereby

recommends that Nitrate Plant No. 1 (an experimental or pilot plant, constructed to use one of the modern fixation processes) be assigned to the Bureau of Chemistry and Soils of the United States Department of Agriculture with an appropriation sufficient to put it in condition for efficient experimental operation and with a suitable quantity of hydro-electric power for its use in chemical and technological research in nitrogen fixation, including the production of nitrates for making fertilizers and other useful products on a scale sufficient for agronomic and other experimentation; that manufacture be adjusted as nearly as possible to experimental and demonstrational needs, and that any product in excess of these needs be sold in accordance with existing law governing the disposal of surplus government property.

*Be It Further Resolved*, that a sum equal to three-fourths of the income received from the sale of power, but not to exceed \$750,000, shall be appropriated, under rules and regulations to be prepared and promulgated by the Secretary of Agriculture after consultation with an advisory committee of seven members, including three representatives of the fertilizer industry, for research in fertilization and plant nutrition and for experimental and demonstration work in the use of fertilizers on the farm, provided that the minimum sum allotted to any state shall be \$8,000, and that the allocation of funds above the minimum to any state shall be made according to the relation of the total cultivated acreage of that state to the total cultivated acreage of the United States; and that a sum equal to one-fourth of the income from the sale of power, but not to exceed \$250,000, shall be appropriated directly to the United States Department of Agriculture to cover the cost of operating Plant No. 1 for research and experimentation, and the Secretary of Agriculture shall conduct such research, or afford facilities for its conduct, within reasonable limits, as may be requested by the Secretary of War or the Secretary of the Navy in the production of nitrates or other materials needed for munitions of war.

*Be It Further Resolved*, that Plant No. 2, the cyanamid plant, shall be kept in standby condition by the Ordnance Department of the War Department for one to three years, in the discretion of the President, for such value as it may have for national defense; that at the end of the period determined the plant shall be sold to the highest bidder, except that the ammonia oxidation or nitric acid part of it may be retained for national defense on recommendation of the War Department;

*Be It Further Resolved*, that all proceeds from sales, whether of property, products or of power (during any period of government operation) shall be covered into the Treasury of the United States as miscellaneous receipts, but shall be earmarked "Muscle Shoals Income," and that funds for conducting the activities recommended herein, including the needs of the War Department for the operation of locks and other structures relating to the Wilson Dam, shall be estimated and budgeted annually in the manner that is customary with other appropriations for the support of the executive departments.

The foregoing suggestions recognize that each of the three major properties at Muscle Shoals presents a separate and different problem. It also recognizes that they are relics of a great war and that

their disposition should follow in general the course that has been followed as to other war-created plants or matériel. Recently scores of wooden ships unfit for use in commerce have been destroyed by the government. But we spent \$3,000,000,000 for ships during the war and are now paying \$120,000,000 a year in interest on that sum. We created an operating deficit of \$1,800,000,000 during the period of government operation of the railroads. Why should we hesitate to scrap an obsolete nitrate plant, to put one hitherto useless into the service of agricultural research, and to put a fine power plant with its accessories on a better income-producing basis pending possible authority from Congress to dispose of it?

#### AGRONOMIC ASPECTS OF THE USE OF AMMONIUM SULPHATE

The farmer's use of ammonium sulphate is too large a topic to discuss in a paper devoted largely to other phases of by-product nitrogen.

Ammonium nitrogen makes a larger demand than nitrate nitrogen upon the lime content of soils to which it is applied. It is of the utmost importance that a proper balance of lime should be maintained in the soil. When it is maintained the complaint occasionally heard about the effect of continued use of sulphate of ammonia disappears. After 40 years of its continuous application on certain experimental fields that have received proper applications of lime, absolutely no injurious effects are observable. Aside from the needed correction in the lime content to balance the lime consumed when sulphate of ammonia is used as a nitrogen carrier, the money spent in supplying lime to the soil is money very well spent indeed for its other effects upon crop production. Cotton, corn, potatoes, sugar-cane, rice and tobacco are among a few of the important crops to which this carrier has been applied with success.

In speaking of the results of the use of any one carrier of nitrogen, I do not in any sense disparage the use of any of the other valuable carriers, particularly nitrate of soda and the newer forms that are now being manufactured from aqua-ammonia, in the synthetic plants of the world. Some are better for one purpose; others for another. All of them promise to find valuable use in agriculture.

# THE UNION CHIMIQUE BELGE SYNTHETIC AMMONIA PLANT AT OSTEND (BELGIUM)

By F. A. F. PALLEMAERTS

*Manager of Research, Division Coke Ovens and Synthetic Ammonia of  
the Union Chimique Belge, Brussels*

This plant was the first to combine the Linde System of coke oven gas fractionation and the Casale Synthetic Ammonia process.

A special process had to be developed to purify the coke oven gas in view of its use for liquefaction, and it was found necessary to make slight alterations in the liquefaction process itself during the early stages of the starting up of the plant. Considerable success was secured after these changes were effected, and the plant is at present producing ammonia with the greatest regularity and at very low cost price.

The success of the Ostend plant was the signal for a rapid increase in the number of similar plants combining the Linde System of hydrogen manufacture from coke oven gas with one of the now classic synthetic ammonia processes. At the present time about a dozen plants of this type are in operation and several others are being planned.

## EXTENSION OF THIS TYPE OF AMMONIA PLANT

Up to the present, the capacity of plants of this type does not exceed a production of 72 tons<sup>1</sup> of ammonia per day, for the reason that gas is not available in sufficient quantity from existing coke oven plants to give larger outputs, and due to the fact that distillation works have not yet been systematically concentrated in Europe. A move is being made, however, in this direction in Belgium, where a series of central carbonization plants is being planned, arranged for generation of power and utilization of gaseous by-products. The first of these central coking plants is to be erected in the southern Belgian coal field (Borinage) and will comprise a synthetic ammonia plant by the U. C. B.-Linde-Casale Systems, the first section of which has a capacity for 72 tons of ammonia a day. It is expected that a second central plant in Hainaut (Belgium) will be completed at about the same time.

<sup>1</sup> 72 metric tons = 79.4 short tons.

## LOW COST PRICE DUE TO USE OF COKE OVEN GAS

The rapid increase in production of synthetic ammonia resulting from the new plants being built or projected, cannot fail to alarm those concerned with the sale of ammonium sulphate, and various theories have been advanced by experts, concerning the possibilities of absorption in quantities as a fertilizer.

The Adriatic Conference which took place a few months ago might be expected to have an effect towards curbing further increases in production, but such is not yet apparent, although it would seem probable that this will come into effect in the future. In the long run, however, the production cost of synthetic ammonia is the factor of greatest importance, and this is where, at least under European conditions, coke oven gas hydrogen scores, for electrolytic hydrogen is either too dear or not available in large quantities in most European industrial countries.

It is indeed generally admitted that in Europe coke oven gas, a by-product and the cheapest gas produced by coal distillation, affords the cheapest source of hydrogen. A comparison of coke oven hydrogen and water gas hydrogen in the case of the Ostend plant showed that the latter costs twice as much as the former.

(Because of special conditions it has been decided to install, in addition to the coke ovens, a water gas plant at Ostend equivalent to the production of ten tons of ammonia per day. The reason is that the Ostend coke oven plant supplies gas to the town, which has large fluctuations in demand, owing to its being a seaside resort with a seasonal population.)

Another comparison was made when it came to choosing between water gas and coke oven gas for hydrogen manufacture in the case of the first coking plant, in Belgium. The same relation in favor of coke oven gas hydrogen was found, and the latter was, of course, decided upon.

This superiority of coke oven gas hydrogen is not necessarily universal, and in localities where very cheap power is available, either in the form of hydroelectric power or in the form of very cheap fuel, such as cheap and good lignite, the use of coke oven gas may not be necessarily the most economic; however, according to our latest information, there is not as yet a single plant where water gas is being produced from lignite for hydrogen manufacture. It appears that the famous Winkler producers of the Badiche (I. G.) at Leuna produce power gas but not water gas, the latter still being entirely made by means of coke.

The following costs are found for 1 cubic meter of hydrogen from different sources, under Belgian conditions, the cost of the process of extraction of the hydrogen from its gaseous prime material *not* being included:

1 cubic meter of hydrogen in water gas<sup>2</sup> (from coke at 170 Belgian francs per ton), 0.22442 Belgian francs,

1 cubic meter of hydrogen in water gas (from coal at 188 Belgian francs per ton), 0.214 Belgian francs,

1 cubic meter of hydrogen in coke oven gas, at 0.14 Belgian francs per cubic meter,

the residual gas being valued at the same price per calorie as the original gas—0.084 Belgian francs.

#### SIZE OF PLANT

The original Ostend plant, which was really experimental as it constituted the first application of the combined Casale-Linde-U. C. B. systems, was built for an output of 12 tons<sup>3</sup> of ammonia per day. It comprised 3 six-ton Casale Units and 3 corresponding Linde Units, one unit of each plant being in reserve.

For the first few weeks of operation, the production was low and irregular, and improvements, bearing almost entirely on the purification of the coke oven gas preliminary to its fractionation, had to be made. Thereafter the production rose steadily, until it reached an average of 18 tons,<sup>4</sup> with peaks of 23 tons, giving a regular output 50 per cent above that for which the plant was intended.

Since then, four additional Casale units has been installed, and the hydrogen plant has been increased by two large units, each of 3000 cubic meters<sup>5</sup> capacity of hydrogen-nitrogen gas; with these, the plant produces 40 to 55 tons of ammonia per day.

A plant of this size is small in comparison with the I. G. plant, the Billingham plant of Imperial Chemical industries, in England, or the

<sup>2</sup> One cubic foot of hydrogen in water gas (from coke at \$4.30 per short ton) costs \$0.0,001,765 per cubic foot; 1 cubic foot of hydrogen in water gas (from coal at \$4.75 per short ton) cost \$0.0,001,685 per cubic foot; 1 cubic foot of hydrogen in coke oven gas at \$0.0,001 per cubic foot, the residual gas being valued at the same price per British thermal unit as the original gas = \$0.000,389.

<sup>3</sup> 12 metric tons = 13.2 short tons; 6 metric tons = 6.6 short tons.

<sup>4</sup> 18 metric tons = 19.8 short tons; 23 metric tons = 25.4 short tons.

<sup>5</sup> 3,000 cubic meters = 105,942 cubic feet; 40-55 metric tons = 44.1-60.7 short tons.

Hopewell plant of the Allied now nearing completion. However, it is proportioned to the size of the country and, as already said, this type of plant especially lends itself to distribution and to economic working, under the conditions found in Europe. When coke oven plants have been concentrated as is now being planned, additional units will be added and favorable results are expected from the enlarged plants.

#### GENESIS OF THE TYPE

When the manufacture of synthetic ammonia was decided upon by the Semet-Solvay & Piette Co. (which has since become a division of the Union Chimique Belge), the first problem was the choice of a cheap source of hydrogen. Coke oven gas was chosen for the reasons already given.

The next question was how to obtain hydrogen from this source.

Several processes were investigated: fractionation, and the iron-steam processes.

The latter processes, which were being worked at the time by Bamag and by the Alais, Froges et Camargue Company, were carefully compared and the conclusion reached that the Alais process, which was carried on in batteries of externally heated retorts, had not been sufficiently proved. The Bamag or Messerschmidt system had been tried out on a good industrial scale, but was found to require a large number of converters of small capacity, considerable labor, and to yield a rather impure hydrogen gas with a low value residual power gas. So these processes were eliminated.

Of the fractionation processes, two were taken under consideration, both elaborated by world-famous firms; they were: the Claude System, and the Linde System.

It would be hazardous to express an opinion on the superiority of either one of these processes over the other, as both have been splendidly worked out in details.

For certain reasons, the Linde process was decided upon.

The principles of each of these systems are too well known to require detailed description here. Briefly, whereas the Claude System applies expansion with external work, by releasing the compressed gaseous mixture in an expansion engine which Claude calls a hydrogen motor, the Linde process utilizes the well known Joule-Thomson effect of self-intensive cooling through expansion without external work.

The Casale System was adopted after a careful study of the three then available processes. The excellence of the choice has been proved by the fact that the Casale System has been adopted all over the world in the face of competition from new processes, and has now reached a daily production of more than 1000<sup>6</sup> tons of ammonia equivalent to 4000 tons of sulphate a day.

Let us now go into the details of the process.

#### PRELIMINARY TREATMENT OF THE COKE OVEN GAS

Such little experience as was available came from a small experimental plant situated at Oberhausen in the Ruhr district, where it had been installed with the collaboration of the Linde Company, by the originator of the coke oven gas hydrogen idea, Mr. Bronn, an engineer of the Rombacher Eisenhütten Company.

All that was known from the Oberhausen experience was that the gas had to be dry and should not contain any carbon dioxide; also that it probably would have to be desulphurized before compression.

These operations had been effected at Oberhausen through purification of the gas in iron oxide purifiers, followed by compression, washing under pressure with water to remove CO<sub>2</sub>, a final decarbonization by means of caustic soda, and drying under pressure by means of calcium chloride.

This treatment was not considered very practical for quantity production and the S. S. P. Co. proposed to replace both desulphurization and decarbonization by an ammonia wash process, working under ordinary pressure. This was accomplished only after some difficulties had been overcome, for the washing of gas with ammonia proved more difficult than might have been expected.

The results of this treatment were excellent, the acid constituents of the gas being removed to the extent of leaving less than 0.1 per cent CO<sub>2</sub>, which is a better result than is obtained with a pressure water wash, the latter leaving as a rule 0.3 to 0.4 per cent CO<sub>2</sub> in the case of the treatment of coke oven gas.

The chemical drying of the gas was omitted and left to the refrigerating plant.

The hydrogen plant was started up along these lines, but difficulties arose from the presence of heavy unsaturated hydrocarbons in the gas; these hydrocarbons polymerized in the less cold parts of

<sup>6</sup> 1,000 metric tons = 1,102 short tons; 4,000 metric tons = 4,408 short tons.

the hydrogen apparatus and caused obstructions and even local explosions. One apparatus was even partly destroyed, and, as a larger unit (3000 cubic meters<sup>7</sup> of  $H_2-N_2$ ) was under construction, the destroyed small unit was not rebuilt.

A thorough investigation of the causes of the trouble was undertaken, and it was decided to install a pressure water wash in order to remove all hydrocarbons which had a solubility coefficient higher than 1.

This proved very effective, and the plant has been running smoothly ever since.

A few incidents of minor importance, however, have shown it desirable to carry the purification process still further, for the purpose of removing oxides of nitrogen and volatile nitro compounds. A simple physical treatment of the gas has been brought into effect, of which excellent results are expected.

The trouble resulting from the formation of explosive copper acetylide has also been eliminated.

The ammoniacal liquor obtained in the decarbonization treatment of the gas is distilled into the sulphate saturators. This simple process will be replaced in future plants by a system of which the ammonia is regenerated for the same purpose, so as to make the whole of the liquid ammonia produced in the ammonia plant available for other uses than sulphate manufacture from sulphuric acid.

Lately, patent applications have been made for a process replacing the whole classical treatment of coke oven gas for the recovery of ammonia and benzol by a new simplified system combined with the synthesis of ammonia. Future coke oven plants built by U. C. B. will in all probability be without saturators or benzol scrubbers in their by-product department.

#### THE HYDROGEN MANUFACTURE PLANT

This plant, entirely built by the Linde Company, is a wonder of industrial physics.

The purified compressed gas is cooled in stages, first in a counter-current cold exchanger, then in a liquid ammonia refrigerator and finally in the fractionation apparatus where the Pictet cycle is applied together with the Joule Thomson effect on nitrogen. This fractionization apparatus is worked out so as to utilize in the most effective way the cold which is contained in the condensed gases which

<sup>7</sup> 3,000 cubic meters = 105,942 cubic feet.

are tapped off at various points on the gas circuit as the temperature is lowered.

The condensates which are successively removed are, in order:

1. "*Ethylene*"<sup>9</sup> at a temperature of about 120° abs. This liquid, although called ethylene, only contains 20 to 30 per cent of  $C_2H_4$ , the other gases being propylene, ethane, methane, and some uncondensed coke oven gas.

2. "*Methane*"<sup>9</sup> at temperatures of 95° to 85° abs.; it contains mainly methane, with ethane, ethylene and uncondensed gas.

3. "*Carbon Monoxide*"<sup>10</sup> a liquid mixture of carbon monoxide and nitrogen with some methane, ethylene, etc.

The compressed cold gas which is left is now a mixture of hydrogen and nitrogen, but still contains small quantities of methane and carbon monoxide.

These impurities are practically totally eliminated by means of a liquid nitrogen wash, which removed methane entirely and carbon monoxide to such an extent as to leave only 1/1000 per cent.

Oxygen and water vapor are also totally removed.

There is no process, to the author's knowledge, which produces such pure hydrogen from any non-electrolytic gas. The CO elimination is far more perfect than with any chemical process, and the chemical elimination of CO by means of cuprous solutions was radically abandoned by the Linde Co. as soon as the liquid nitrogen wash had been applied.

<sup>9</sup> The mean composition of this "ethylene" is the following:

	per cent
$C_2H_4$ .....	30.6
$C_3H_6$ .....	6.1
$C_2H_6$ .....	30.6
$CH_4$ .....	30.6
CO.....	2.0

<sup>9</sup> Composition of the "methane":

$CH_4$ .....	74.4
$C_2H_6$ .....	1.9
$O_2$ .....	1.2
CO.....	9.6
$H_2$ .....	4.2
$N_2$ .....	8.7

<sup>10</sup> Composition of the "carbon monoxide":

CO.....	18.0
$O_2$ .....	2.0
$CH_4$ .....	6.9
$N_2$ .....	73.1

## COST OF LINDE COKE OVEN GAS HYDROGEN

The two main factors in the cost of Linde coke oven gas hydrogen are energy and the cost of the coke oven gas itself.

The energy consumption per cubic meter<sup>11</sup> of hydrogen supposed at atmospheric pressure is 0.246 kilowatt hour.

The total expenses for the production of 1.3 meters of hydrogen (without nitrogen and at atmospheric pressure) amount to 0.141 Belgian franc or to \$0.0039.

The cost of the coke oven gas which is used, obviously depends on the available market or on the assumption which is made as to its value.

In certain cases, when there is no sale for coke oven gas and where its cost price is taken as the difference between coal plus operation expenses and total income from by-products, it may be considered as having little or no value.

This case is unusual, however, and is daily becoming more so.

Taking the case of the Ostend plant, where gas is sold to the city gas distribution company at the same price per kilogram calorie as coal, the cost of gas comes in as follows:

$$2.3 \text{ meters}^{12} \text{ of coke oven gas at } 0.14 \text{ Belgian francs} = 0.323 \text{ Belgian francs}$$

However, as the Linde process returns 70 per cent of the calorific power of the gas in the form of a high calorific power gas at 6500 to 800 Kcal per cubic meter;<sup>13</sup> and when allowance is made for the income from this source, counting the hydrogen-free gas at the same price per K calorie as the original coke oven gas, the detail is as follows:

$$30/100 \times 0.323 = 0.0969 \text{ Belgian francs, or } 0.27 \text{ American cents}$$

And the total cost of Linde coke oven gas hydrogen is therefore

$$0.395 + 0.27 = 0.665 \text{ American cents per cubic meter}$$

The author does not know of any lower cost for hydrogen.

<sup>11</sup> The energy consumption per cubic foot of hydrogen supposed at atmospheric pressure is 0.00698 kilowatt hour.

<sup>12</sup> 2.3 cubic meters at 0.14 Belgian franc = 81.2 cubic feet = \$.0039.

<sup>13</sup> 6,500 to 800 Kcal per cubic meter = 731 to 90 British thermal units per cubic foot.

## UTILIZATION OF RESIDUAL GAS

In this calculation, the residual high power gas, which consists mainly of methane and ethylene and their homologues, with some nitrogen, has not been valued at more than the original coke oven gas per calorie. This is a fair assumption as long as it is not used for any other purpose than coke oven gas itself is used. But this gas is much more valuable than coke oven gas; because, first, it is entirely free of all sulphur compounds, impurities, and absolutely anhydrous. It also is particularly suited for certain industrial uses, such as the heating of special furnaces, (the Libbey Owens process for instance), and it also lends itself remarkably well to long distance conveyance of gas which is being developed in continental Europe. A simple calculation shows that one million K calories represent 121 cubic meters of rich residual gas at 8,270 Kcal or 214 cubic meters of ordinary coke oven gas at 4680 Kcal. The compression to 30 atm. of these volumes, which is generally admitted as being suitable for long distance distribution, will require 25.4 hp. in the case of the former gas, as against 45 hp. in the case of the latter. The energy economy will therefore be 43.5 per cent in favor of residual gas.

## VALORIFICATION OF RESIDUAL GASES

The above advantages concern only the crude uses of the rich residual gas. This gas, however, lends itself to even more valuable applications, for its different components can be collected separately and used in a whole series of chemical processes to form valuable products.

*Ethylene* can be turned into ethyl alcohol or into ether, (this application has already been put into practice in certain European plants) into diethylsulphate, or into any of the valuable halogen addition products. Propylene, which accompanies its lower homologue, can be transformed into its corresponding alcohol in the same process.

It may be mentioned that the Linde Company builds ethylene fractionating apparatus which will turn the 30 per cent "Ethylene" obtained in the ordinary Linde coke oven gas fractionating apparatus into 80 to 95 per cent ethylene, the latter gas being thus rendered suitable for chemical processes where ethylene of high purity is required. The ordinary 30 per cent ethylene can be used as such (without rectification) in a good many processes, and especially in alcohol and ether manufacture.

A Linde ethylene fractionation apparatus has been installed by the I. G., and another will soon be working at the Ostend plant of the U. C. B.

*Methane* has not found any considerable industrial use up to the present, and it is merely used for heating purposes. A certain amount, however, is compressed into tubes and used for oxy-methane steel cutting and for the soldering of steel, lead etc. A small quantity of hydrogen has to be mixed with the methane in order to increase the velocity of combustion, which is too slow in the case of methane alone. This use will probably never account for the whole of the production of methane in coke oven gas hydrogen plants; but there is no doubt that additional uses for methane will sooner or later be found, probably in the direction of its polymerization into liquid hydrocarbons.

It may be said that already one utilization of methane is becoming industrial. It consists in cracking methane into hydrogen and carbon dioxide, by the action of steam and the use of suitable catalysts. This transformation, which at first sight may seem a degradation, has its use in cases where a large quantity of hydrogen is required from a small quantity of coke oven gas. Indeed, whereas one volume of coke oven gas will yield half a volume of hydrogen, the same quantity of coke oven gas will give:

*1.7 volumes of hydrogen or more than 3 times more*, if methane is converted into hydrogen.

As the process makes it possible to make three times more ammonia from the gas of a given battery of coke ovens, it will be apparent, the advantage is considerable even without a remunerative use for methane.

It must not be forgotten, however, that in this case there is little residual gas left for heating the ovens, which have to be supplied with some other gas, such as producer gas, and the latter gas, as a rule, is more expensive per calorie than coke oven gas, under European conditions.

It will be seen from the above that it may be anticipated that the above price based on the residual gas having the same value as the original coke oven gas, will be lowered to a considerable extent if the various constituents of the residual gas are exploited to the advantage they might be.

## DESCRIPTION OF THE OSTEND TYPE OF COKE OVEN HYDROGEN PLANT

Coke oven gas from the adjoining coking plant, which has undergone the usual treatment for by-product recovery, is extracted by means of exhausters and submitted to a treatment in which it is successively washed with an ammonia solution, with water in sufficient quantity to remove the ammonia carried over, then with sulphuric acid, which eliminates the last trace of ammonia, and finally with caustic soda which acts as a drier and which fixes any sulphuric acid or carbonic acid which might be left in the gas.

The purified gas is stored in a gasholder, from which it is exhausted by compressors which compress it in two stages to about 9 atmospheres.<sup>14</sup> Under this pressure it is refrigerated by means of liquid ammonia from the synthesis plant, and, in passing through a cold exchanger it is warmed up again to about normal temperature.

At this temperature it is now washed with water in pressure water wash towers, where one volume of compressed gas is washed with a little more than one volume of water. The older towers pass about 1750 cubic meters<sup>15</sup> of gas per hour, the new towers passing about 5300 cubic meters<sup>16</sup> and the corresponding quantities of water.

The energy of the water as it leaves the pressure towers is recovered in hydraulic turbines placed on the same shaft as the pumps and motors, each group comprising motor, pump and turbine. The motor has to do all the work at the start, but its power consumption falls to about 40 per cent when the water is admitted through the turbines.

This water evolves gas as soon as it has passed the turbine, like soda water in a bottle when the stopper is removed. This gas is collected and returned to the residual gas from the fractionation. The "degasification gas" is not all carbon dioxide as in the case of the Haber-Bosch water wash, where a gas with 30 per cent CO<sub>2</sub> is pressure washed. Indeed, the gas here, besides containing originally only 1 to 2.5 per cent CO<sub>2</sub>, has been very completely decarbonated in the ammonia wash. The object here is entirely different, and seeks to remove mainly acetylene present in the proportion of *4 parts per thousand* only. It seems ridiculous to have to resort to such powerful means in order to remove a disagreeable gas present in such minute

<sup>14</sup> 9 atmospheres = 132 pounds per square inch.

<sup>15</sup> 1,750 cubic meters = 61,800 cubic feet.

<sup>16</sup> 5,300 cubic meters = 187,000 cubic feet.

quantities, but the treatment is effective besides being absolutely necessary, until some better means is brought into action.

As it is, the "degasification gas" has the following composition:

	<i>per cent</i>
Olefines.....	9
Oxygen.....	1
Carbon monoxide.....	5
Hydrogen.....	25
Methane.....	30
Ethane.....	2
Nitrogen.....	10

There is no other use for this gas than to incorporate it into the residual gas used for heating purposes.

Coming back to the coke oven gas, which is now without benzol and amply purified, it is refrigerated for the second time by means of cold exchangers and ammonia refrigerators to a temperature of about  $-45^{\circ}$ . At this temperature water vapor is removed sufficiently to avoid rapid obstruction of the fractionating apparatus due to freezing of the condensed water. The gas now enters the fractionating apparatus and leaves the latter, on the one hand, as a pure mixture of hydrogen and nitrogen with the desired nitrogen percentage for the ammonia synthesis, and, on the other, as various "residual" gases which at present are mixed and, after cold exchange, returned to the coking plant where the joint residual gas is used to heat the batteries of coke ovens.

These coke ovens, which are of the U. C. B. (Semet-Solvay & Piette) combined type are arranged for being heated by producer gas, rich gas, or any intermediate gas. The most varied gaseous mixtures depending upon the demand for gas from the town gas distribution company, which they also supply, are used successfully. Sometimes some coke oven gas is used but the normal food is a variable one consisting of producer gas, (from U. C. B. automatic producers gasifying coke breeze) and rich residual Linde gas. The ovens work splendidly on this variable but well controlled mixture. They have been working for nearly four years now under these conditions.

Returning to the compressed coke oven gas, the story of the water wash is rather interesting. As mentioned already, no provision was made for its use in the original plant and there was a certain amount of trouble with the fractionation plant, when a large quantity

of benzol was collected at the ammonia refrigerators portion of the fractionation apparatus. When the water wash plant was set working, there was no longer any benzol to be seen, proving that the whole of the benzol was dissolved by the pressure water, which acted more effectively than any oil wash. So it was at once decided to install a second refrigerator before the water wash, and so benzol was again recovered. This system of benzol recovery does not consume any energy or materials, as it simply consists of static refrigerators and cold exchangers and runs on liquid ammonia from the synthesis plant.

Since the Ostend plant has been started, the Linde Company has built a number of installations, treating daily in all *more than*  $2\frac{1}{2}$  *million* cubic meters<sup>17</sup> of coke oven gas. Besides the extensions to these various plants under preparation, or already being carried out, as at Ostend, several large new installations have been planned. The earliest plants, except for the experimental unit at Oberhausen, were built first in Belgium and then in France, but of late several large ones have been erected in Germany. It now looks as if the Germans, who apparently at first were content to rely on the I. G. process, are seriously entering the field with the Linde coke oven gas hydrogen process.

In all, the Linde Company has provided 7 units of 1,600 cubic meters<sup>18</sup> of coke oven gas per hour, and 19 units of 5,000 cubic meters<sup>19</sup> per hour, all for ammonia synthesis. One unit for treating 7,500 cubic meters<sup>20</sup> of gas per hour is under construction, which will supply hydrogen for the Bergius process.

It is worthy of notice that the Linde hydrogen-nitrogen process does away with the expensive combustion of hydrogen in air, which is applied in certain plants, in order to incorporate the necessary amount of nitrogen into the gaseous mixture. Linde nitrogen costs only 0.2 kilowatt hours per cubic meter in the larger unit, and it would be necessary to secure hydrogen for nothing in order to justify using one volume of precious hydrogen in order to obtain 2 volumes of nitrogen.

In the  $H_2-N_2$  apparatus, the nitrogen, besides coming partly from the coke oven gas itself, is introduced by saturation of the hydrogen

<sup>17</sup>  $2\frac{1}{2}$  million cubic meters = 88 million cubic feet.

<sup>18</sup> 1,600 cubic meters = 56,500 cubic feet.

<sup>19</sup> 5,000 cubic meters = 175,800 cubic feet.

<sup>20</sup> 7,500 cubic meters = 265,000 cubic feet.

with nitrogen during the liquid nitrogen wash. The nitrogen proportion is ingeniously regulated by acting on the temperature of the gas, the pressure being kept constant. The temperature itself is regulated by the pressure under which liquid nitrogen is kept in the liquid nitrogen boiler, which constitutes the last stage in the cooling of the gas.

A pressure of about 0.2 atmospheres in the nitrogen boiler ensures the required nitrogen percentage in the mixture, the gas itself being under 9 atmospheres.

It has been found useful at Ostend to generate hydrogen with a little less than 25 per cent of nitrogen, and to correct the mixture in each synthesis unit by means of an addition of nitrogen.

The Ostend nitrogen machines are of a size corresponding to the hydrogen units. They produce pure nitrogen of 99.8 per cent purity and at the same time pure oxygen at 99 per cent. The Linde Company builds much larger units than the Ostend ones, the largest unit making 3,600 cubic meters of nitrogen per hour (126,000 cubic feet per hour). In one plant, 16,000 cubic meters (560,000 cubic feet) of nitrogen are produced per hour.

#### THE AMMONIA SYNTHESIS PLANT

It is a Casale plant.

The Casale system has become very widely distributed in Europe, in Russia and Japan. Above 1,000 tons<sup>21</sup> of ammonia a day are produced by it. This shows very remarkable development, as the first Casale unit, which produced 2 tons of ammonia per day, was started at Turin in Italy only in the autumn of 1921. From 2 tons the capacity of the Casale unit was increased successively to 6, 20 and to 30 tons. Altogether *24 plants* are at present in operation, distributed all over the world: 10 in France, 3 in Japan, 6 in Russia, 1 in Spain, 1 in Switzerland, 2 in Belgium (where another large plant is being planned), 3 in Italy, 1 in England, 1 in the United States (it was originally erected at Niagara Falls but it is now being transferred to Belle, Charleston, W. Va.)

The Casale Synthesis plant runs on hydrogen from any source; 9 plants run on coke oven gas hydrogen, 10 on electrolytic, 3 on water gas hydrogen.

The equipment is standardized so that a 6-, 20- or 30-ton a day Casale unit can be purchased complete.

<sup>21</sup> 1,000 metric tons = 1,102 short tons.

At Ostend there were at first three 6-ton units; at present there are seven. In the new plants which are being planned by the U. C. B. Company, 30-ton units are contemplated; although no unit of this size has yet been built. The experience with the 20-ton unit, which is in action in several plants, and which has an output of 26 to 32 tons, (actually reached in one of the Japanese plants), shows that a production of 35 to 40 tons may be expected of the 30-ton unit.

When the new large unit goes into operation it will, to the best of the writer's knowledge, be bigger than any ammonia unit, including the Haber-Bosch I. G. unit.

As is well known, the Casale process works under a pressure of 750 atmospheres.<sup>22</sup> Of late, it has been thought in various quarters that it was advantageous to carry out the synthesis at lower pressures, in the order of 200 atmospheres<sup>23</sup> or even less. In the writer's opinion, there is much to be said against this view, as the use of high pressure has very decided advantages. One of the most important of these is that the *whole* of the ammonia output is available in the form of liquid ammonia, the latent cold content of which is extremely useful and permits very considerable energy savings in other parts of the plant, especially where coke oven gas has to be treated. The elimination of the huge refrigerating machines from the necessary plant which follows in the absence of available liquid ammonia alone constitutes a considerable economy of energy, as has been mentioned in the description of the coke oven gas treatment. The availability of the total output in the form of liquid ammonia also renders complete debenzolization possible without any appreciable energy consumption, and besides, there are still other uses of this liquid ammonia in the modern ammonia derivatives plant, such as refrigeration of the nitrous fumes in the ammonia oxidation nitric acid plant, etc., which make the liquid state of the Casale ammonia an extremely valuable asset to the process.

As regards power consumption in compressing the gas, it has been repeatedly shown that there is very little difference in the energy consumed once the pressure exceeds 200 or 300 atmospheres. For instance:

The ratio of the energies required for compressing an ideal gas to 729 and to 243 atmospheres is 6 to 5, so that whereas the Casale

<sup>22</sup> 750 atmospheres = 11,000 pounds per square inch.

<sup>23</sup> 200 atmospheres 2,940 pounds per square inch.

process consumes 1.2 kilowatt hours per kilogram<sup>24</sup> of  $\text{NH}_3$  for compression, a process working under 300 atmospheres will still consume 1.05 kilowatt hours. This difference, small as it is, is compensated for by the absence of a recirculating pump in the Casale cycle, recirculation being induced in the latter system by the injection of the fresh gas, under a drop of about 50 atmospheres pressure.

When the further energy savings resulting from obtaining all the ammonia in the liquid form is added, the advantage of the Casale system as regards power consumption is obvious.

(The above comparison is easily worked out when it is remembered that the isothermal compression energy is proportional to the *logarithm* of the pressure.)

The high pressure equipment of a Casale unit is so compact that it weighs far less than any unit of the same capacity working under a so-called medium or low pressure.

At Ostend the hydrogen-nitrogen mixture produced in the Linde hydrogen plant is sent into a gasholder, from where it is exhausted by the compressors. These compressors (there are six of them) each compress 1,000 cubic meters<sup>25</sup> of hydrogen-nitrogen mixture per hour; (it must be remembered that they are the smaller type of unit). The compressed mixture is admitted *as such*, without any purification or desiccation, into the synthesis cycle, which comprises an oil separator, a synthesis tube, a water cooled condenser, and a condensate receiver. Recirculation at Ostend is still being effected in most of the units by means of recirculation pumps, but the latter is being replaced by a new injector system which considerably simplifies the circuit and does away with the upkeep and attendance, as well as power consumption, necessitated by these pumps.

Further simplifications have been brought in at the pioneer plant at Terni, which is run as an experimental plant by the S. I. R. I. Company, this company being the research organization of the Casale Company and founded by Dr. Luigi Casale. These simplifications consist in the elimination of the oil separator, (as a result of the suppression of the recirculation pumps) and in the incorporation of water cooled ammonia condenser and condensate receiver into one single apparatus. The two 5-ton units working under this

<sup>24</sup> 1.2 kilowatt hour per kilogram = 0.543 kilowatt hour per pound, pressure 300 atmospheres = 4410 pounds per square inch. 1.05 kilowatt per kilogram = 0.477 kilowatt hour per pound.

<sup>25</sup> 1,000 cubic meters = 35,314 cubic feet.

system at Terni are beautifully simple and occupy the small space of 12 x 30 feet, for the two compressors.

Compressors at Ostend have been modified in order to be able to receive their hydrogen as it comes directly under the pressure of 9 atmospheres from the Linde fractionating apparatus. This arrangement permits of a further energy saving amounting to one-third of the compression energy, so that the power requirement is reduced from 1.22 to 0.82 kilowatt hours<sup>26</sup> per kilogram of  $\text{NH}_3$  in the 6-ton units, and to 0.76 kilowatt hours in the 20 ton units, the process becoming thus from day to day more economical.

It has been suggested to apply some further purification to the compressed hydrogen before admitting it into the synthesis tube; but apart from the fact that any serious attempt in this direction would complicate the process, there would be little advantage in prolonging the activity of the catalyst, as its replacement is only a matter of a few hours. Besides, there is no object in prolonging the life of the catalyst beyond a year, as it is not advisable to let a catalysis tube work for more than a year without testing its mechanical condition.

The most beautiful part of the Casale system is the catalyst tube, which is so arranged that the pressure tube, which is very similar to a big naval gun, is kept at a temperature at least 100 below the temperature where the alteration of the structure of the metal under the effect of hydrogen begins. The efficiency of the Casale design is shown by the fact that a catalysis tube, which had been in continuous action for three years, was tested at *1500 atmospheres*<sup>27</sup> and withstood the test.

This remarkable result is achieved through disposing the circuit of the gases inside the tube in such a way as to have the inside surface of the pressure tube cooled by the incoming cold gaseous mixture, which in the course of its progress takes up part of the heat of the hot gases as they leave the catalyst. The latter is contained in an annular space in the core of the tube, and is thermally insulated from the inside wall of the pressure tube by the concentric heat exchanger and the cold gas which enters the tube. This arrangement, which is protected by several Casale patents, has proved wonderfully effective.

<sup>26</sup> 1.22 to 0.82 kilowatt hour per kilogram = 0.553 to 0.372 kilowatt hour per pound  
0.76 kilowatt hour per kilogram = 0.344 kilowatt hour per pound.

<sup>27</sup> 1,500 atmospheres = 22,050 pounds per square inch.

It is interesting to note that the reaction is regulated in an ingenious way. As under 750 atmospheres pressure the violence of the catalytic reaction would be such as to overheat the catalyst, there is left in the reaction mixture sufficient uncondensed ammonia as to keep the system just slightly endothermal, so that it may be regulated by means of an electrically heated resistance placed in the axis of the catalyst tube, and over which the gases pass just before entering the catalyst, after they have been heated by temperature exchange with the gases which leave the catalyst. In practice the current tension and intensity are kept constant, the speed of recirculation being regulated so as to maintain temperatures and maintain regular production. The energy consumed by the resistance is from 0.27 to 0.18 kilowatt hour per<sup>28</sup> kilogram  $\text{NH}_3$ .

The presence of the necessary quantity of uncondensed ammonia in the gaseous mixture before catalysis is insured by simply water-condensing the reaction gases. No simpler means could be devised.

It is apparent that the system as a whole is marked by the utmost simplicity, as all special condensation arrangements are controlled with artificial refrigeration and no special purification treatment of the gas, either catalytic or chemical, is necessary.

### THE CATALYST

The efforts of Dr. Casale have tended towards producing a cheap and robust catalyst rather than a delicate low temperature catalyst. The process of manufacture, which has been patented, consists in burning steel turnings of a given composition in oxygen, in the presence of certain activators which are introduced in the form of certain very cheap materials. The temperature at which the combustion in oxygen takes place is so high as to drive off any phosphorus or sulphur. When all the metal is burnt and the oxide solidifies, the mass is allowed to cool and is then broken up and crushed into pieces of a proper size. The catalyst is introduced in the form of an oxide, and is reduced in the catalyst tube by means of hydrogen-nitrogen mixture.

Catalyst which has lost some of its activity is regenerated in the same way. This catalyst, which is made of the cheapest materials, enters into the cost price of the ammonia to the extent of a fraction of a cent only per kg. of ammonia.

<sup>28</sup> 0.27 to 0.18 kilowatt hour per kilogram = 0.122 to 0.0813 kilowatt hour per pound.

It would be wrong to think, though, that this catalyst is not very active. It is, at any rate, remarkably free from sulphur as analyses show it contains one-fourth the sulphur of a reputed specially active catalyst used in a recent American process.

The writer hopes it will not be considered out of place if a tribute is here paid to the originator of this simple and effective synthetic process, Dr. Luigi Casale, who, while a student at the University of Padua, undertook the study of what was then, except for Dr. Haber's work, an entirely new subject; and carried through its industrial application with the most meagre financial support to a successful conclusion.

The death of Dr. Casale, two years ago, was a great loss to the scientific and industrial world, for he no doubt would have made further important contributions to the advancement of knowledge in synthetic processes.

Fortunately, however, the effect of his example inspired his disciples and collaborators who now carry on his work so that progress has not stopped at his death, as is shown by the numerous improvements which have since been made and the synthetic methanol process now working at Terni (producing five tons per day).

#### THE SULPHATE PLANT

It is an easy matter to transform liquid ammonia into sulphate by the use of sulphuric acid, but it is difficult to do so in a simple way without using complicated devices such as mechanical stirrers in the saturators, or blowing air or gas into them for different purposes such as has been successfully developed by the U. C. B. Co. Some difficulties with this method were, at first, encountered, due partly to the high temperature maintained in the saturators, and to the large production per unit capacity of the apparatus. But these troubles were in a short time overcome, and now 100 tons of sulphate are made per day in one small saturator of about 9 feet diameter.

This sulphate is whizzed and perfectly neutralized with ammonia in a special way, and is then dried in a rotary drier by means of combustion gases from a coke furnace.

This method of manufacturing sulphate will soon be replaced at Ostend by a new process similar to the gypsum process. The system, which is covered by a series of U. C. B. patents, is special in that it uses an ammonium carbonate solution made in a new way from combustion gases of a central pulverized coal boiler plant. It will

be remembered that there is no concentrated  $\text{CO}_2$  available in the coke oven gas hydrogen process as there is in the Haber-Bosch process, so that a different source had to be used. Although this sulphate process produces sulphate at a lower cost than from sulphuric acid, it is only operating on a small scale at Ostend, notwithstanding that the U. C. B. Co. is the largest sulphuric acid manufacturer in Belgium, because the prime material used is a valueless by-product of another industry of the U. C. B.

Another new feature, also patented, is that the evaporation of the concentrated sulphate solution, which is the most expensive item in the "Gypsum" process, has been done away with and replaced by a simpler precipitation process.

A series of other developments are being experimented with at the Ostend plant, which is used as a pilot plant by the U. C. B. Company in its researches upon the new synthetic industries.

To summarize, a new approach to the synthetic ammonia manufacture problem has been opened up that in practice has proven remarkably satisfactory and cheap. Its development has in turn made possible a series of derived processes, mainly concerned with the transformation of the various residual gaseous by-products of coke oven gas. Among these several new fabrications have been attacked such as those of the fatty alcohols and of some of their derivatives.

## DISCUSSION

C. J. RAMSBURG (The Koppers Company, Pittsburgh, Pa.): I think that the first two papers this afternoon by MacDowell and by Brand have been fine. They related to the question of the disposal of nitrogen after we get it, and a great deal of good has been gained from them, but owing to the lateness of the hour the discussion of this other very important paper by Pallemmaerts should now come before the meeting.

DR. H. A. CURTIS (Yale University, New Haven, Conn.): There is one question that occurs to me regarding the cost of sulphate, which I believe Dr. Pallemmaerts did not state. Was sulphuric acid included in estimating your ammonium sulphate?

DR. PALLEMAERTS: The price of the sulphuric acid and the transformation of ammonia into ammonium sulphate amounts to about 400 francs per metric ton (\$10.12 per 2000 pounds) of ammonium sulphate. That is about 4 francs per kilogram of ammonium sulphate (\$0.05 per pound).

DR. CURTIS: The figures, I understand, include all of the capital cost as well as your operating cost.

With regard to the price of coke oven gas, does the price you have given us represent approximately the price at which you would turn over your coke oven gas to the city?

DR. PALLEMAERTS: It is exactly the price at which we are offering the gas to the city.

DR. CURTIS: You are not taking advantage of a higher price for the coke oven gas when its calorific value has been increased by hydrogen removal

DR. PALLEMAERTS: The plant really comprises two plants, the synthetic ammonia plant and the coke oven plant, with separate bookkeeping, and the synthetic ammonia plant buys from the coke oven plant its gas at the price of 14 centimes per cubic meter of gas at 4,250 calories, (\$0.111 per thousand cubic feet of gas at 479 B.t.u. per cubic foot) and the residual gas is being turned back to the coke oven plant at the same price per 4,250 calories.

DR. CURTIS: Do those figures include any royalties?

DR. PALLEMAERTS: They include royalty to the Casale system.

DR. CURTIS: That is an unknown figure; or is it something that would be public information?

DR. PALLEMAERTS: I do not know it myself. I do not think there would be any objection to publishing it, but I do not know the figure myself.

CHAIRMAN PARSONS: I think everybody is so astonished with the success of your plant, which appears to be so much better than any other plant they have ever heard about, they are a little backward in talking about their own figures.

DR. PALLEMAERTS: It must be understood that these figures apply to local conditions, and that is why I began by putting you on your guard about not applying those figures to American conditions, because they have to be examined thoroughly before they can be applied to American conditions.

DR. CURTIS: The labor costs would make quite a difference.

CHAIRMAN PARSONS: I do not suppose that the labor costs are so much, because it is run largely by machinery anyway.

DR. CURTIS: I have a feeling that these costs are no doubt about accurate for Belgium, but before you really got through translating them into American costs you would not arrive at figures much different from those with which we are familiar.

MR. RAMSBURG: May I read something from the paper here to try to clear it up, because I believe it would be of interest to everybody to have one fixed point in their mind about this cost of gas.

"Taking the case of the Ostend plant where gas is sold to the city gas distribution company at the same price per kilogram calorie as coal, the cost of gas comes in as follows: 2.3 cubic meters of coke oven gas at 0.14 Belgian francs cost 0.323 Belgian francs."

I am trying to make out of that at what price you are selling the gas in cents per thousand cubic feet. Have you an answer to that?

DR. PALLEMAERTS: Yes, I can work it out very quickly. Eleven cents per thousand cubic feet.

MR. RAMSBURG: That would be 11 cents a thousand for 470 British thermal units per cubic foot.

R. B. MOORE (Dean of Science, Purdue University, Purdue, Ind.): I have the figures on the relative value of labor in Belgium and in the United States. These are, of course, arbitrary figures. Electricians in Belgium 70 cents; in the United States \$7.78. Coal miners in Belgium 95 cents; in the United States \$5.58. Common labor Belgium 65 cents; in the United States \$2.59.

CHAIRMAN PARSONS: Have you any idea of the approximate labor factor which comes into your total?

DR. PALLEMAERTS: At the rate of 20 per cent I think. The cost of labor is undoubtedly lower in Belgium than in the United States. I think labor in Belgium earns about 35 francs a day, which is about one dollar a day. That is the common laborer, and I think that men of that sort earn about four dollars a day in the United States.

It must not be forgotten that in Belgium in the same plant we have many more men so that the product of the number of men by what they earn is not at all in the same proportion as the proportion of the actual salaries. That brings down the difference, you see.

C. H. MACDOWELL: Do you remember the cost of coal at the coal plant?

DR. PALLEMAERTS: The coal costs about 177 francs per metric ton. (\$4.48 per 2000 lbs.)

MR. MACDOWELL: What is the value of that particular coal?

DR. PALLEMAERTS: That would be coal at 6,400 calories per kilogram, (11,520 B.t.u. per lb.) and the cost of that is about \$4.90 per metric ton, (\$4.48 per 2000 lbs.).

CHAIRMAN PARSONS: You certainly can get coal cheaper than that at many of the coke plants in this country.

MR. E. C. EVANS (National Federation of Iron and Steel Manufacturers, Caxton House, East, Tothill St., London, England): Does the Ostend Cor-

poration take the gas return from the synthetic ammonia system at 800 B.t.u.? I have seen somewhat similar systems in Germany recently, and we are considering the possibility of installing a plant in Great Britain. One of our troubles is that the gas company makes use of gas at 500 B.t.u. and this system returns the gas at something like 800 B.t.u. The gas companies do not want to dilute it and the people who want to put up the synthetic ammonia plant do not want to dilute it.

I would like to know what means have been adopted at Ostend to meet that condition.

DR. PALLEMAERTS: It happens that most of the residual gas is used in heating the coke ovens. The coke ovens utilize a mixture of three gases according to the demand for the gas of the town. A mixture of two or three gases is being used for heating the coke ovens, either producer gas or excess coke oven gas or residual gas, and it is very easy to regulate the U.C.B. system of coke ovens with that gas.

MR. C. G. ATWATER (The Barrett Co., New York City): You should take out all your hydrogen first. Then you put the residual gas back again into your coke oven gas.

MR. EVANS: What are you to dilute the gas with? There is no producer gas at present. At one plant I have seen they are diluting the gas with nitrogen down to 500 B.t.u. value and are using that gas in the coke oven. Another question: What are your power costs?

DR. PALLEMAERTS: The cost per kilowatt is 0.18 Belgian francs. That is just about half a cent per kilowatt hour.

MR. ATWATER: Your cost of sulphate of ammonia is 1.94 Belgian francs per kilogram?

DR. PALLEMAERTS: The cost is 1.94 Belgian francs per pound (\$0.055) of sulphate.

MR. MACDOWELL: How important an item in the cost of coal is the freight from the field; the cost of freight from the mine to the coke plant?

MR. PALLEMAERTS: The distance is about 69 miles from Belgian coal, but it is mostly English coal which arrives directly from England.

MR. DAVID L. JACOBSON (The Koppers Co., Pittsburgh, Pa.): What are the small nitro-compounds that still give some difficulty? Do you use liquid nitrogen to take the carbon monoxide out? What do you do with the liquid nitrogen after the carbon monoxide is absorbed?

DR. PALLEMAERTS: The liquid is collected as a solution of carbon monoxide and methane in nitrogen, and it is about 80 per cent nitrogen and the rest

carbon monoxide and methane. At present we are mixing that gas, after its heat has been made use of, with the rest of the residual gas, but in certain cases it would be advantageous to collect that gas apart and either use it or not use it, and in that way enrich the residual gas up to 8,400 calories, (944 B.t.u. per cubic foot).

MR. JACOBSON: What about the nitrogen compounds?

DR. PALLEMAERTS: The nitrogen compounds are mostly all unsaturated nitrogen compounds. We have not investigated very far, but we have heard that methods of preventing them from going into the liquefaction apparatus have been developed.

MR. RAMSBURG: May I ask one question of Mr. MacDowell? He says in his paper that nitrogen is the most expensive plant food the farmer has to purchase. I think that is a very unwise statement to go into this paper to be published in connection with Mr. MacDowell's business or our business. I think it either ought to be amplified or removed.

PROFESSOR TRINKS (Carnegie Institute of Technology): I am not a chemist but I know there is argon in the atmosphere. What happens to that?

DR. PALLEMAERTS: When liquefying air a certain quantity of the argon is eliminated in the apparatus. There is a special process which eliminates the rare gases of nitrogen and the nitrogen is liquefied without it.

# THE MANUFACTURE OF SYNTHETIC AMMONIA BY MONT-CENIS PROCESS

BY RUDOLPH BATTIG

*General Director, the Mont-Cenis Process, Westphalia*

*Read by Willibald Trinks, Professor of Mechanical Engineering, Carnegie  
Institute of Technology*

Coal mining is in a bad way, and this state of affairs will undoubtedly continue, unless completely new solutions of the economic problem are found. To-day, it is no longer a question of obtaining sufficient coal, but of disposing of the coal brought to the surface.

From an unbiased standpoint it may be stated, that since the introduction of coking and, as a next stage—the development of by-product recovery, nothing radical has happened up to the time of the recent liquefaction of coal gas and low temperature carbonization.

One of the most important by-products recovered in coking, namely, coke oven gas, has been used almost exclusively as a source of heat for furnaces or boilers, without considering the most latent value contained in this gas.

If we consider the composition of coke oven gas, we see at once that the most valuable part, the hydrogen, is present to a degree corresponding to one-half of the volume of the gas. The problem of the economic extraction of hydrogen has been solved in several ways. In Germany the most satisfactory and economical method is the one of the Linde Eismaschinen Gesellschaft in Munich. I should like to mention, that this firm is working in close connection with the Gasverarbeitungsgesellschaft in Herne-Sodingen, Westphalia, which has developed the so-called Mont-Cenis process and is using this method.

The still further development of coking chemistry will as a matter of course, include other valuable components of the gas and I believe that I am not going too far if I prophesy, that coke oven gas will gradually become so valuable a substance, that its direct burning as a source of heat will become out of the question save perhaps in special circumstances, among which I may include the piping of gas to great distances from the source. I think further, that I am not saying too much in affirming, that the whole depressed condition of the mining

industry should, by virtue of the new revenues gained by the utilization by coke oven gas, be able to return to prosperity. The most important method of using coke oven gas, consists in the manufacture of ammonia, a field in which I have had the privilege to work.

If we consider it possible—as has been mentioned by several people—that a nitrogen factory will be built beside each coking plant, the thought must arise, whether the world demand for nitrogen may not become more than saturated. The problem is, however, not such a simple one. From a technical standpoint there is of course a possibility of building a works for the daily fixation of sixty tons of nitrogen alongside of each plant, producing a thousand tons of coke a day. In practice, it should however not be forgotten, that a nitrogen factory producing about twenty thousand tons of fixed nitrogen per annum, costs a considerable sum of money, namely, under present German conditions about thirteen to sixteen million marks, or about three to four million dollars, depending upon the conversion into ammonium sulphate or ammonium nitrate, this amount being sufficiently large to render practicable the building of such a plant only in places which appear suitable by reason of high hydrogen content of the coke oven gas and a reasonably cheap supply of power.

On the other hand it should not be forgotten, that the nitrogen consumption of the world is increasing year by year by an enormous amount.

I have summarized the most important figures on hand of official statements and have completed them from archives of the different banks. They show the possibilities for nitrogen on the world market, especially if the food problem becomes more serious in view of the enormous increase of population.

The increase of the world consumption amounts, figured in percentage of each previous year, from 1913 to 1928—about five and one-third per cent per annum on an average, and from 1923 to 1928 twelve per cent yearly.

The subject may also be viewed from the following standpoint. The increase in the world consumption of nitrogen is covered almost exclusively by synthetic nitrogen products, which gradually are displacing all other sources of nitrogen, especially Chile saltpetre, which to-day is second in the world production.

This condition is based on the lower production cost of nitrogen fixed by synthesis. Although the price of Chile saltpetre has been

lowered recently because of a decrease in the export duty and by a subsidy from the state, it cannot compete favorably for any length of time, with synthetic nitrogen. The difference in the price is too considerable.

TABLE I  
WORLD PRODUCTION AND WORLD CONSUMPTION OF NITROGEN IN FERTILIZERS

YEAR	PRODUCTION
1913	771,000 t N
1923	945,000 t N
1924	1,057,000 t N
1925	1,250,000 t N
1926	1,198,000 t N
1927	1,400,000 t N
1928	1,679,000 t N (approximately)

DISTRIBUTION OF THE PROSPECTIVE NITROGEN PRODUCTION FOR THE  
DIFFERENT COUNTRIES (FOR THE YEAR 1928)

COUNTRY	DISTRIBUTION
Germany.....	about 700,000 t N
Chile.....	about 420,000 t N
England.....	about 144,000 t N
United States.....	about 130,000 t N (30,000 t of it synthetic)
France.....	about 70,000 t N
Italy.....	about 44,000 t N
Norway.....	about 30,000 t N
Japan.....	about 29,000 t N
Poland.....	about 28,000 t N
Canada.....	about 28,000 t N
Belgium.....	about 24,000 t N
Sweden.....	about 8,000 t N
Czecho-Slovakia.....	about 7,000 t N
Holland.....	about 7,000 t N
Jugo-Slavia.....	about 6,000 t N
Australia.....	about 2,000 t N
Spain.....	about 2,000 t N
Total amount.....	about 1,679,000 t N

It is improbable, that also other forms of fixed nitrogen will be able to compete with synthetic nitrogen.

This is true especially of the obsolete method of fixation from air by the arc process, which, with a current consumption of over sixty

TABLE II  
NITROGEN CONSUMPTION OF FERTILIZER IN FRANCE

YEAR	CONSUMPTION
1923	71,000 t N
1925	107,000 t N
1926	110,600 t N

NITROGEN CONSUMPTION OF FERTILIZER IN ITALY

	1921	1924	1926
	<i>t</i>	<i>t</i>	<i>t</i>
Chile saltpetre.....	5,000	7,000	7,600
Calcium nitrogen.....	3,400	9,400	13,000
Sulphate of ammonia.....	4,100	7,900	13,300

CONSUMPTION AND IMPORT OF NITROGEN IN FERTILIZER IN JAPAN

YEAR	CONSUMPTION	IMPORT
1912	18,000 t N	16,600 t N
1913	23,400 t N	22,000 t N
1915	10,000 t N	4,000 t N
1918	10,600 t N	2,000 t N
1920	30,000 t N	14,200 t N
1923	50,000 t N	28,800 t N
1925	67,000 t N	40,400 t N

YIELD OF THE CROPS AND NITROGEN CONSUMPTION IN GERMANY, HOLLAND  
AND BELGIUM

	WHEAT	RYE	POTATOES	SUGAR BEETS	CONSUMP- TION
	<i>t/ha</i>	<i>t/ha</i>	<i>t/ha</i>	<i>t/ha</i>	<i>kg.N/ha</i>
Germany.....	1.87	1.46	13.4	25.0	14.0
Belgium.....	2.67	2.38	19.38	30.0	35.4
Holland.....	2.84	2.08	16.75	33.7	42.9

INCREASE OF NITROGEN CONSUMPTION IN GERMANY

YEAR	NITROGEN PER HA CULTIVATED LAND
1913	6.0
1925/26	11.7
1926/27	13.8
Minimal amount required according to experts.....	21.0
Normal amount according to experts.....	40.0

kilowatt hours per kilo of nitrogen, is only practicable where cheap power is available, as for instance in Norway, where however, the factories are at the present time reconstructed on modern lines. Similar conditions exist, if not to the same degree, for calcium

TABLE III

PART CHILE SALTPETRE TAKES IN THE [WORLD PRODUCTION, IN PERCENTAGE

	1913	1914	1925/26	1926/27
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
By-product recovery.....	36.7	40.0	26.0	28.0
Chile saltpetre.....	50.0	54.0	30.0	16.0
Synthetic ammonia and calcium cyanamide.....	7.1	6.0	44.0	56.0

## WORLD CONSUMPTION OF CHILE SALTPETRE

YEAR	CONSUMPTION
1913	421,450 t Nitrogen or 2,719,000 t saltpetre
1924/25	368,500 t Nitrogen or 2,377,000 t saltpetre
1925/26	329,400 t Nitrogen or 2,125,000 t saltpetre

## PRICE OF CHILE SALTPETRE C.I.F. HAMBURG BEFORE REDUCTION

	ABOUT	RM 1.54 PER KILOGRAM OF NITROGEN
	<i>per cent</i>	
This includes:		
Production cost.....	32	RM 0.49
Transportation to coast.....	24	RM 0.37
Export duty.....	20	RM 0.31
Freight.....	8	RM 0.12
Administration expense and petty costs.....	16	RM 0.25
	100	RM 1.54

Calculating on a possible decrease of the production cost of 50 per cent by rationalizing, the price might be reduced about RM 0.25 to..... RM 1.29 per kg. N.  
 Price of synthetic ammonia on the world market (London quotation) about..... RM 1.00 per kg. N.

cyanamide, in which a high current consumption is added to a considerable cost for coke and lime.

It would seem, therefore, that there can be no question, that the future belongs to the catalytic synthetic ammonia process. More-

over, the absorption of the products of such processes by the world market is, in view of the low manufacturing costs in <sup>the</sup> comparison

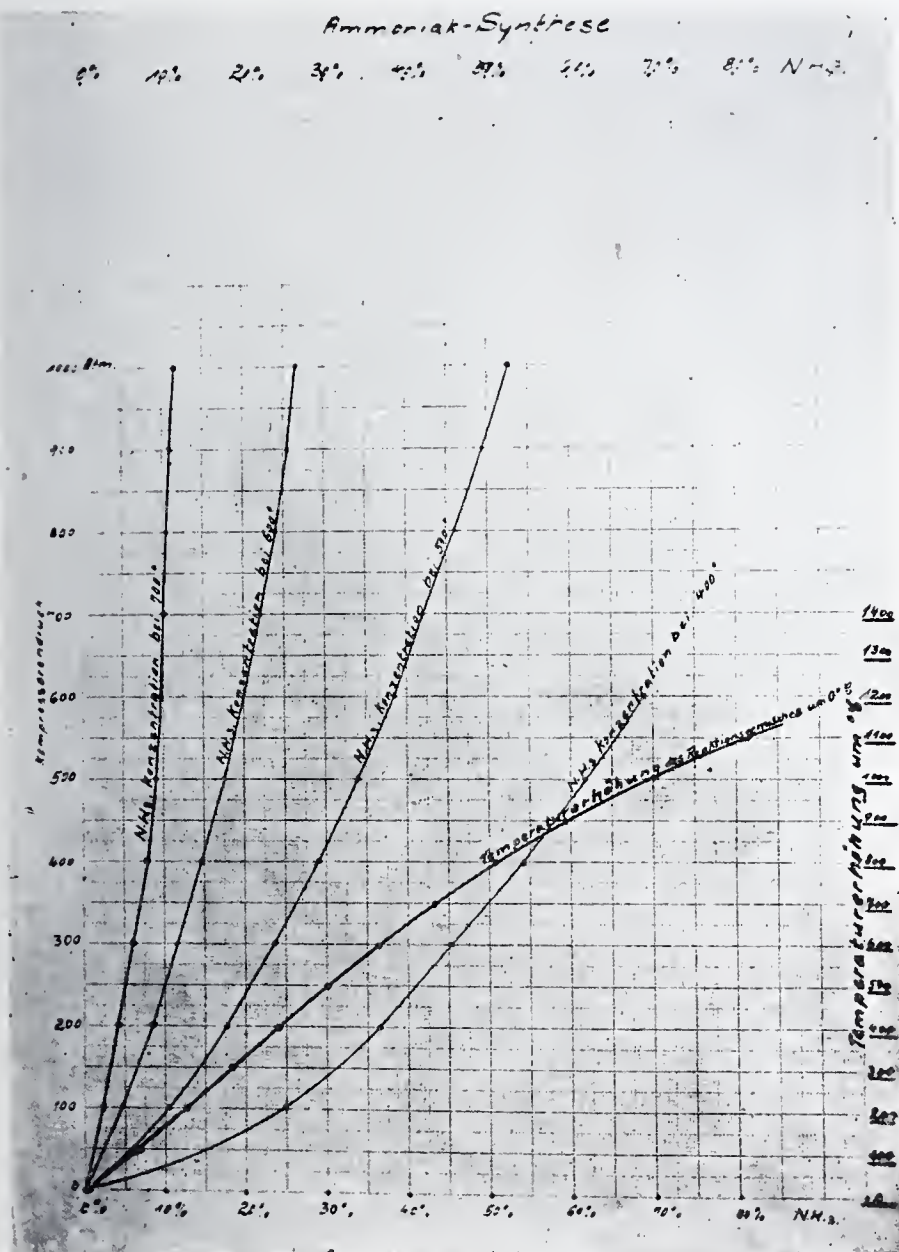


FIG. 1. CURVE OF EQUILIBRIUM OF THE AMMONIA REACTION

with other processes, in the near future practically limited only by consideration of the capital cost.

I would like to add that the erection of new nitrogen factories has kept pace with the increased consumption, and there is no danger that the factories, existing in all countries and those now under construction might lead to an overproduction of nitrogen.

In the second part of my paper, I propose to deal in this connection with the synthetic ammonia process as developed at Mont-Cenis. The synthesis of ammonia is, as you know, based on the combination of nitrogen and hydrogen by the aid of catalysts at high temperatures and pressures to ammonia, from which the nitrogen for the fertilizers is gained, either by combination with sulphuric acid or by oxidation and neutralization to ammonium nitrate. You will also know, that the synthesis was for many years accompanied by the greatest difficulties, since these elements have little affinity for each other. Conversion to ammonia takes place only to a quite small degree and at high temperatures, by virtue of the position of the equilibrium.

At lower temperatures a far more complete conversion is possible on theoretical grounds; but the reaction takes place so slowly, that technically valuable yields of ammonia per unit of time are not obtained. Two methods exist for increasing the degree of combination: in the first place, the use of high pressures; and secondly, the employment of certain substances, so-called catalysts, which accelerate the reaction in such way that technically possible yields are obtained even at lower temperatures. The employment of high pressures changes the equilibrium in the sense of a greater conversion to ammonia and thus equalizes to a certain extent—the unfavorable action of high temperatures. Within a temperature range of five hundred to seven hundred degrees centigrade and a pressure range of two hundred to four hundred atmospheres, the theoretically possible ammonia yield increases almost proportionally with the pressure, while this proportion sinks rapidly with increasing temperature.

The existing processes for the synthesis of ammonia differ only in their combination of the three factors; temperature, pressure and catalyst.

Another important part in the application of these processes is the profitable production of hydrogen, while the production of nitrogen itself only plays a minor part with regards to the cost price.

The starting material for nitrogen in our process is air, which is separated by means of the well-known Linde low-temperature process, whereby oxygen forms a salable by-product. The production of nitrogen by means of the Linde process is extremely cheap and the capital cost runs very low.

*Seitnahme von synthetischen Ammoniak aus Luft und Wasserstoff, der Ammoniak zu Chlorsalz oder zu Ammoniumsulfat (1. Schritt) (2. Schritt)*

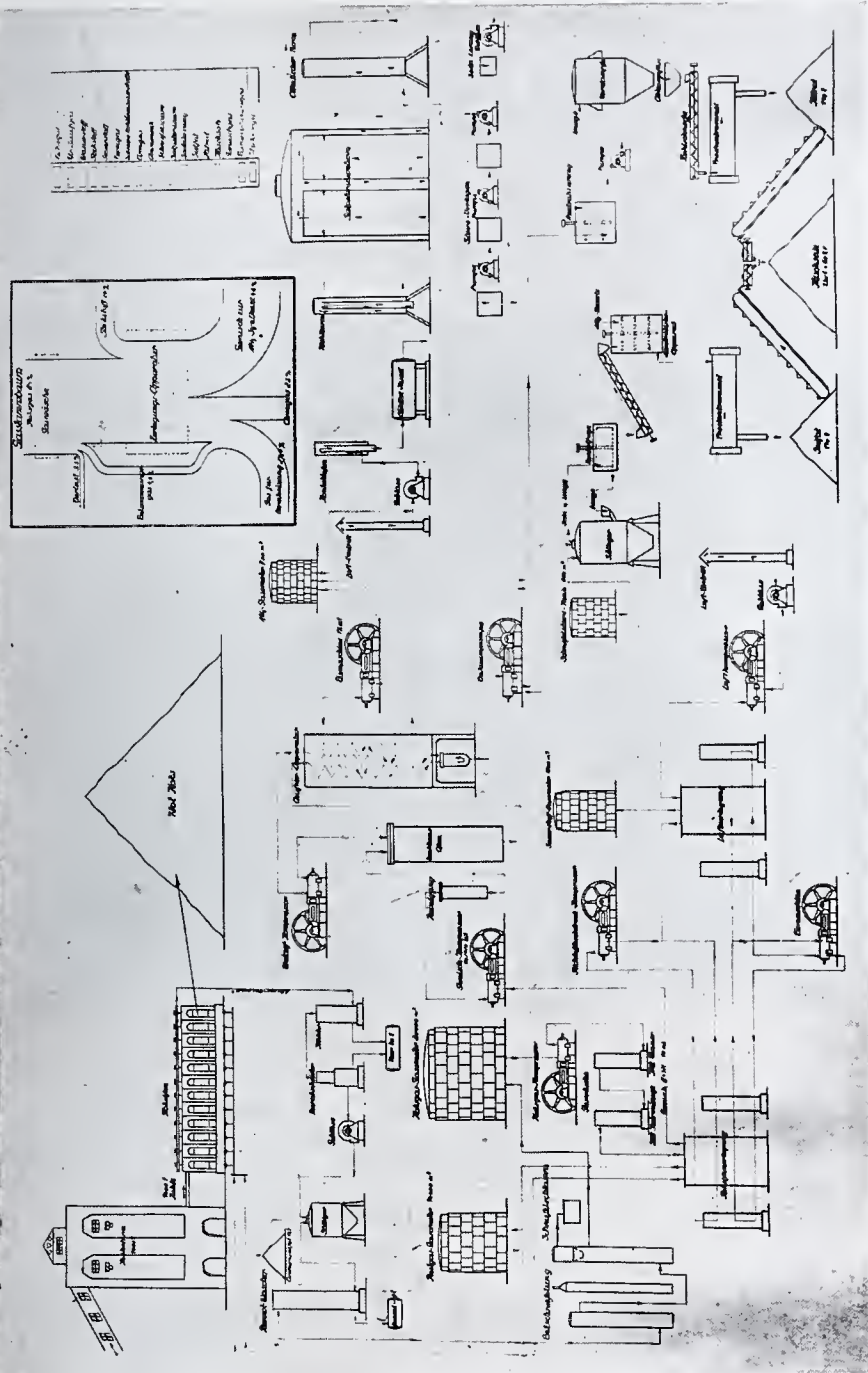


FIG. 2. SCHEMATIC DIAGRAM OF MONT-CENIS PROCESS—PRODUCTION OF SYNTHETIC AMMONIA FROM BY-PRODUCT COKE OVEN GAS AND AIR AND CONVERSION OF AMMONIA INTO AMMONIUM SULPHATE AND AMMONIUM NITRATE

For the production of hydrogen in connection with the Mont-Cenis process any source of hydrogen, including water itself may be used. Since we have come to discuss new uses for coal, we are mainly interested in the production of hydrogen from coke oven gas, a method that is also used in our plants. I should like to say a few words about the profitable use of the different methods for the production of hydrogen. The current consumption for the electrolysis of water is relatively high, amounting to four to four and one-half kilowatt hours per cubic meter of hydrogen, that is about thirteen kilowatt hours per kilogram of nitrogen. In addition to this one and a half



FIG. 3. VIEW OF THE LARGE NITROGEN PLANT AT MONT-CENIS

kilowatt hours have to be added for the synthesis of ammonia itself, so that the total amount of a works of this sort amounts to fourteen to fifteen kilowatt hours. Even if you consider, that the electrolysis of water gives the purest of hydrogen available, so that expensive chemicals are almost unnecessary, the electrolysis of water is practicable economically only in those places, where very cheap hydroelectric current is available. This question, however, does not concern us.

Another method for the production of hydrogen, is the Haber-Bosch process. It employs a mixture of producer gas and water gas containing about thirty per cent of hydrogen, twenty-two per cent

of nitrogen, thirty-seven per cent of carbon monoxide, and four per cent of carbon dioxide. The carbon monoxide is converted, by admixture of steam and passage at atmospheric pressure and at a temperature of about five hundred degrees over an iron catalyst, into carbon dioxide and hydrogen. This method is not at all cheap and hydrogen produced in this way cannot compete economically with hydrogen gained by separation of coke oven gas in connection with the Linde process. Lately, coke, which was used in very large

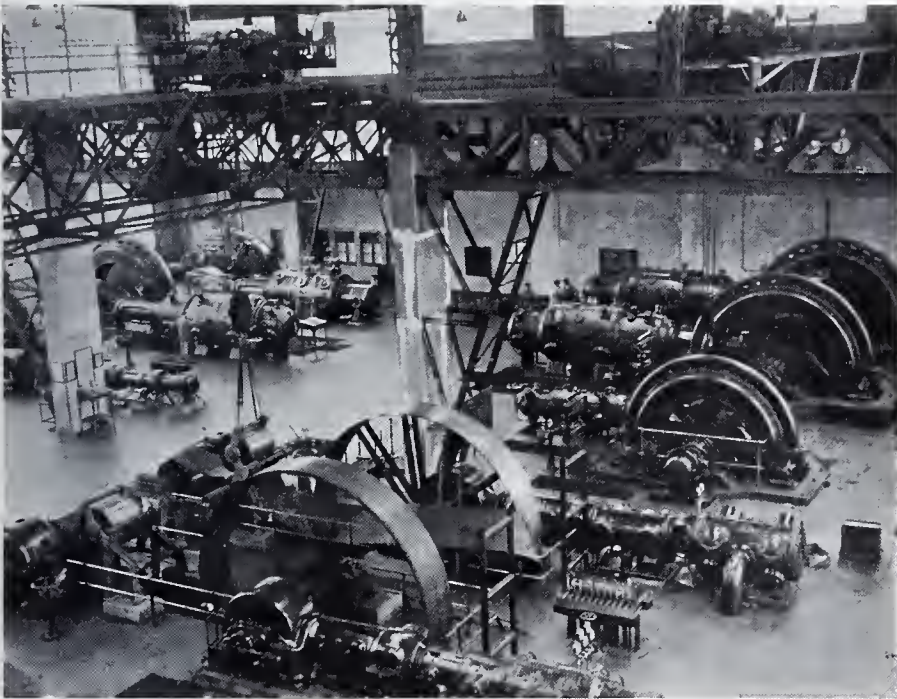


FIG. 4. INSIDE VIEW OF THE LARGE ENGINE HOUSE

quantities, is being replaced by lignite briquettes, by which means the whole process is considerably cheapened.

The latest method, which in every respect seems to offer most favorable prospects, consists in the manufacture of hydrogen from the by-product coke oven gas. This gas, as is well known, is produced in enormous quantities as a by-product of the coking of coal. Its average hydrogen content is from 45 to 55 per cent. The separation of this hydrogen is carried out at Mont-Cenis and the Hibernia works in Westphalia, where for the first time in Germany, coke oven gas has been used for the manufacture of hydrogen, by means of the

Bronn-Linde low-temperature method, which in practice gives very pure hydrogen. The method of separation is as follows:

Coke oven gas, after being free from tar, ammonia, benzol and sulphur in the ordinary way, is compressed to twelve atmospheres. It consists of fifty per cent of hydrogen, twenty-two to twenty-four per cent methane, six per cent carbon monoxide, two and a half per cent unsaturated hydrocarbons, three to four per cent carbon dioxide, eight-tenths per cent oxygen and about sixteen per cent of nitrogen. The compressed gas is freed from carbon dioxide by washing

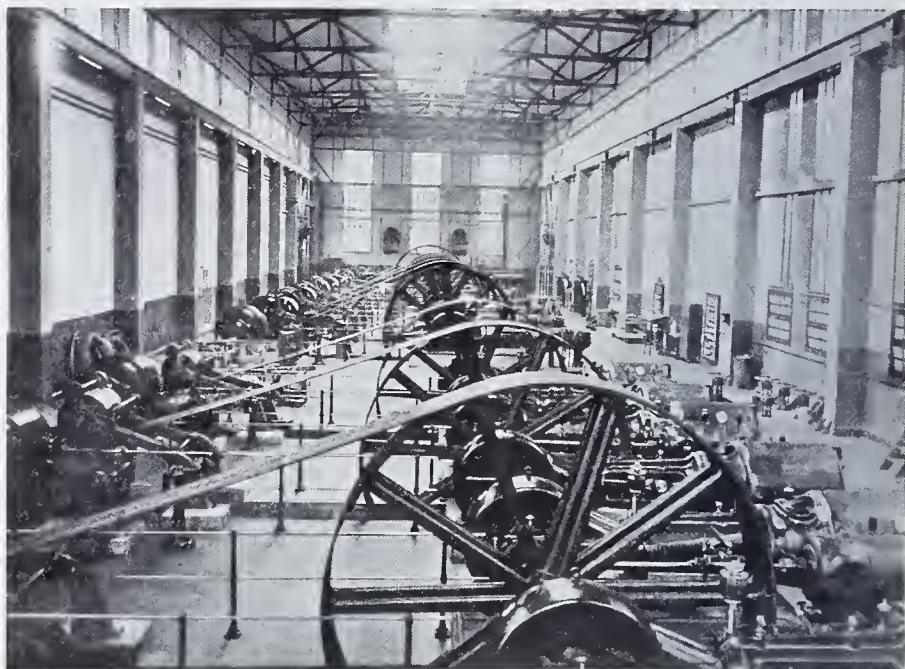


FIG. 5. VIEW OF CIRCULATION PUMPS

with high pressure water and finally with caustic soda. It is then separated into its components by a low temperature method in a similar manner used for air. In the process of separation the unsaturated hydro-carbons condense first, then the methane and finally the carbon monoxide. Any remaining carbon monoxide is washed out at minus one hundred and ninety degrees centigrade by means of liquid nitrogen. The gases are cooled by means of a counter-current exchanger, through which the cooled fractions flow in the opposite sense further by means of ammonia machines, and by virtue of the evaporation of liquefied fractions in the separator itself, as

well as finally, by means of nitrogen compressors, which operate a circuit in which the gas is compressed to one hundred and fifty atmospheres and allowed to expand. Liquid nitrogen is thus obtained which—as already mentioned,—is used for the final washing of the coke oven gas and for freeing this from any remaining traces of carbon monoxide. During this washing, part of the nitrogen evaporates and forms, by mixing with the hydrogen separated from the coke oven gas, a mixture of nitrogen and hydrogen which by regulating the addition of nitrogen, can be adjusted in such way as to be of the required proportion for the synthesis of ammonia.

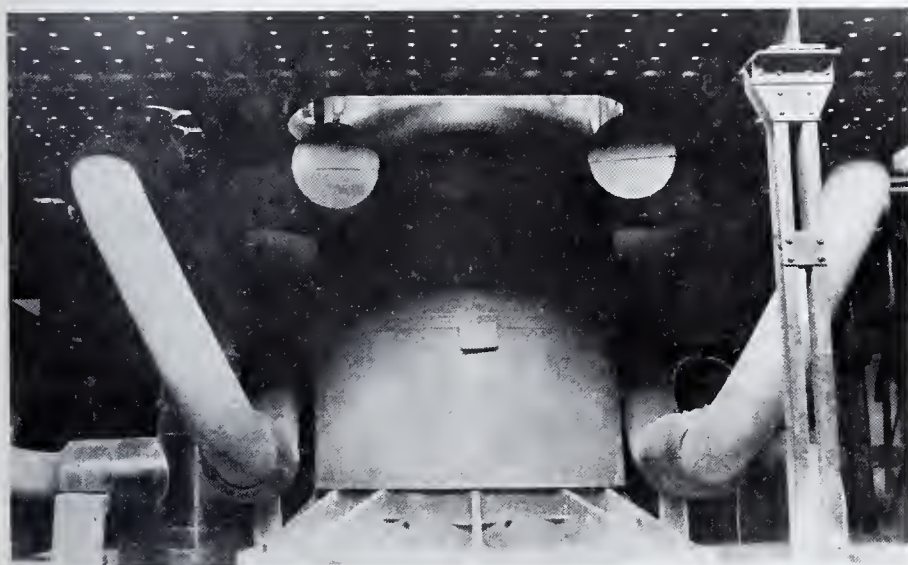


FIG. 6. CONTACT FURNACE

The fractions separated by liquefaction from the coke oven gas, which consist principally of an acetylene fraction, a methane fraction and a carbon monoxide fraction, can either be collected separately, or in one gasholder as so-called "Restgas," which contains about the whole calorific value of the original coke oven gas, less that of the hydrogen, which is available for heating and other purposes, and the losses during separation. These are extremely small and amount at the most to two and a half per cent of the calorific value of the coke oven gas treated. These losses occur during the final de-gassing of the pressure washing water, since, in addition to carbon dioxide, other components are dissolved in the water.

If the three fractions are collected separately, both the acetylene and the methane fraction can be utilized for the manufacture of further quantities of hydrogen by means of a thermal cracking of these hydrocarbons. If the acetylene and methane fractions are mixed, a so-called rich gas, having a heating value of seven thousand calories per cubic meter, that is about eight hundred British thermal units per cubic foot, is obtained. The other gases constitute a so-called poor gas, which is made up of the carbon monoxide fraction and the gas recovered from the pressure water. The gas which re-



FIG. 7. VIEW OF SYNTHESIS HOUSE FROM THE SIDE OF THE LEAD BATHS

sults by mixing all these fractions "Restgas" has a calorific value of four thousand, five hundred to five thousand three hundred German calories per cubic meter.

In this connection a possibility of great interest may be mentioned, namely the piping of this gas to consumers at a distance, whereby the economical range of a piping system becomes greatly increased, since it follows, that the cost of pipe lines for a gas of seven thousand calories must necessarily be much less than for a gas of four thousand two hundred calories.

I now come to a discussion of the synthesis proper, especially as carried out at Mont-Cenis.

When Haber and Bosch began their epoch making work on the introduction of synthetic ammonia into chemical industry, they had before them the task of employing pressures greater than any which had formerly been used. In this, however, they were successful after protracted trials. Their plant worked under a pressure of two hundred and thirty atmospheres, at five hundred and thirty degrees centigrade. All other workers, who have tried to make ammonia after the Haber-Bosch method, have had as their object the attainment of higher yields per passage, that is to say in essence, they have aimed at a better heat economy by means of higher and higher pressure; the percentage of ammonia obtained per passage is not so important. *One great factor* is the space-time-yield, that is to say, the figure which expresses the yield of ammonia per litre of catalyst per second. But *the most important* factor is the loss of heat and gas during the whole process.

These considerations point to two different methods of working: on the one hand, the higher the pressure, the smaller the apparatus; but it must not be forgotten, that at one thousand atmospheres, even a small leak will cause a high loss, compared to a lower pressure. Moreover, the gas does not obey completely the simple laws at such high pressure, especially with regard to compressibility. The fact is that they lead to high yields, but they bring with them increased working difficulties, increased losses and increased costs, of which the compression to one thousand atmospheres in place of one hundred is only one. The repairs of such a plant, working with a gas weighing about two-thirds of the weight of water, would naturally be much higher than one, working with lower pressure.

While all other known processes have chosen the way of higher pressures, without any important decrease in temperature, we have had the good fortune to take an important step forward in the other direction, namely in decreasing the pressure and at the same time the temperature. Our process offers the possibility of working at low pressures and temperatures, and by means of highly active catalysts, whereby high yields of ammonia are obtained. The process contains therefore something that is quite new, considering all other methods. It moves the synthesis to a temperature region of four hundred degrees centigrade and to a pressure region of under one hundred atmospheres. We are in a position, at such low temperatures and

pressures, to obtain just as high and even higher yields than those given by other processes. The reason for this lies in the employment of especially highly active catalysts, which give high yields even at the above named low temperatures and pressures. As a result, an essential advantage of the process consists in the simplification of the whole plant. It should be noted, that a pressure of one hundred atmospheres lies in the region of modern steam practice.

Further the low pressures employed makes possible another advantage, which up to now, has not been used by any other process, namely that the heat, which comes from the reaction, is destroyed in the reaction space itself. This leads to a very uniform temperature throughout the whole ammonia converter.

Consider for a moment, what it means to produce one thousand kilos of ammonia per hour. The heat evolution per kilogram of nitrogen amounts to six hundred and sixty calories, equal to two thousand six hundred British thermal units, so that six hundred and sixty thousand calories, equal to two million six hundred thousand British thermal units, are developed in the converter, and have to be dissipated. It will be understood that these one thousand kilos of ammonia are for the most part formed just from those portions of the gas which contain relatively little ammonia, namely in the upper part of the converter, where the gas enters. In other words, there occurs here a great accumulation of heat, which must be dissipated. It will be seen therefore, that a low pressure process has the great advantage of permitting the installation of heat exchanger in the furnace itself, thus obtaining a high degree of uniformity of temperature within the catalyst mass, a principle, which we have worked out very well.

The course of the synthesis is as follows: The mixture of hydrogen and nitrogen is compressed to ninety or one hundred atmospheres, and heated in exchangers to about three hundred to three hundred and fifty degrees centigrade. It then passes, after purification, into the conversion furnaces which contain the catalyst. As already mentioned, the reaction heat is in general sufficient to maintain the necessary reaction temperature of about four hundred degrees. While in almost all other processes the heating for starting the apparatus is done by electricity and so on, that is from an outside source, this is not necessary with the Mont-Cenis process. In this process the necessary heat is supplied by the gas only, which for starting, is brought to the required temperature in

ordinary furnaces. Nitrogen is added as a heat carrier to avoid any danger. The reaction gases—after partial combination to ammonia in the furnace, pass through the heat exchangers and are then further cooled, the ammonia being obtained in liquid form, under such conditions that practically no ammonia remains in the circulating gases. The gas mixture, after elimination of ammonia, is re-circulated through the contact furnaces by means of circulation compressors. By regulating the velocity of circulation, it is possible to regulate the percentage of ammonia formed per passage within wide limits. This regulation causes the whole process to be extremely elastic, since, at a relatively high velocity of circulation, the yield per passage drops, while the space-time-yield increases to a higher degree. This method allows the compensation of any variation, which may be caused, for instance,—by changes in the volume of available hydrogen, due to irregularity in the delivery of coke oven gas, water gas and so on, further in connection with any irregular supply of hydro-electrolytic hydrogen. The liquid ammonia, which is formed in the condensers, is expanded and evaporated, whereupon it is converted into sulphate or nitrate.

The advantage of the Mont-Cenis process over all other methods may be summarized in the following: The advantages consist in the employment of low pressures and temperatures and in the decrease in the plant and operating costs, and in the simplification in the whole working, which is thereby made possible. The low pressure reduces gas losses to a minimum. It requires moreover a minimum amount of repairs to plant, machines and so on. The heat economy is regulated in a very advantageous way, since heating is only required during the starting of the plant and since the use of exchangers has been developed in unusual detail. The furnace needs no starting by means of electric heating and so on. The construction of the furnaces allows an extraordinarily uniform regulation of temperature within the catalyst mass. The life of the catalyst is such that a change is very seldom necessary. We have already observed a catalyst life of over eight months; and the cost for the catalyst is therefore diminished to a fraction of one pfennig per kilo of nitrogen. The whole method of working is distinguished by its smoothness and security. The best proof for this is the fact, that at this very hour the second large plant for the coking plant of Mont-Cenis and Hibernia is being started.

The combination of the Mont-Cenis process with the Bronn-Linde

plant for the manufacture of hydrogen allows the utilization of coke oven gas on the largest possible scale with very favorable yields of hydrogen, so that practically no losses occur. The use of highly active catalysts allows the attainment of high yields of ammonia. The yield per passage may be regulated within wide limits, by which means a great elasticity of the whole system is introduced as a compensation for variations in supplies. The separation of the ammonia is carried out by cooling to a low temperature, according to a special method, with almost complete utilization of all cold, by which means a practically complete separation of the ammonia from the mixture is obtained.

I should like to explain once more in a few words the course of our process as shown in the schematic diagram (Page 209). The coke oven gas, which comes from the coke ovens, goes through the usual process of purification by separation from tar, ammonia and benzol. It is then freed from sulphur, passes through the gasometer and from there flows to the coke gas compressors, which compress the gas to twelve atmospheres. Under this pressure the gas is freed from carbon dioxide by washing with water. It finally reaches the proper coke gas separation, where the finished mixture of hydrogen and nitrogen is formed. This mixture is compressed to about one hundred atmospheres in the high pressure compressors. It then passes into the reaction furnace. The mixture which leaves the reaction furnace is freed from ammonia in the cooling tower, while the remaining mixture is pumped back to the furnaces by circulating compressors. The vacuum pump releases the ammonia and presses part of it to the sulphate plant, and part of it to the nitrate plant. The production of sulphate is carried out in the ordinary way. In the nitric acid plant the contact furnace is shown where the ammonia is oxidized in contact furnaces then the boilers for the utilization of the accumulated heat, finally the nitric acid tower, the neutralization—evaporation—and drying plants. The nitrate, which has formed, is mixed with sulphate.

In conclusion I wish to suggest another consideration in order to show the importance of the combination of a nitrogen factory with a coal mine from the standpoint of the increase in the productive value of the mine. In other words, I want just to show you to what an enormous degree the value of each ton of coal is increased by means of utilization in this way of the hitherto so often neglected coke oven gas.

Let us assume, that a mine has an output of one million tons of coal, which it sells in the ordinary way. The price for coal in Germany, is at present thirteen marks and seventy pfennig. The same plant with a coking plant and by-product recovery would increase its productive value to eighteen marks and ninety pfennig.

TABLE IV

INCREASE OF THE PRODUCTION VALUE OF A COLLIERY UNDER GERMAN CONDITIONS

1. With coal production only:	
1,000,000 t coal.....	= RM 13.70 per ton of coal raised
2. With coking plant and by-product recovery:	
Coal.....	about 570,000 t at a value of about RM 10.4 million
Coke.....	about 335,000 t at a value of about RM 6.2 million
By-products (tar benzol, ammonia sulphate).....	20,500 t at a value of about RM 2.3 million
Total production value.....	RM 18.9 million or RM 18.90 per ton.
3. With coking plant, by-product recovery and ammonia plant:	
Value of the production including coke and by-products according to Figure 2.....	
	RM 18,900,000.0
Added to this 20,000 t Nitrogen at RM 830 per ton.....	RM 16,600,000.0
Total production value.....	35,500,000.0 or RM 35.50 per ton

COMPARISON OF THE PRODUCTION VALUE AND THE CAPITAL COST

	CAPITAL COST PER TON OF PRODUCTION	INCREASE OF THE CAPITAL COST IN PERCENTAGE		PRODUCTION VALUE PER TON OF PRODUCTION	INCREASE OF THE PRODUCTION VALUE IN PERCENTAGE	
		Case	Per cent		Case	Per cent
Case 1.....	RM 40.0	1:2	25	RM 13.70	1:2	40
Case 2.....	RM 50.0	2:3	30	RM 19.20	2:3	84
Case 3.....	RM 65.0	1:3	62	RM 35.70	1:3	157

If it be assumed that the same mine adds a nitrogen factory for the working-up of coke oven gas, all the above figures for the value of the products remain unaltered, but there has to be added a production of about three hundred cubic metres of coke oven gas per ton of coking coal, that is to say, from four hundred and thirty thousand tons about one hundred and thirty million cubic metres of gas or three hundred sixty thousand cubic meters per day, equal to twelve million

seven hundred thousand cubic feet per day. If we calculate on an average content of available hydrogen of forty-five per cent, the volume of hydrogen, which may be separated from the coke oven gas, is one hundred and sixty-two thousand cubic metres, equal to five million seven hundred and twenty thousand cubic feet per day. This separation can be carried out without in any way disturbing the heating of the coke ovens, since the rejected gas which contains two-thirds of the original calorific value, is sufficient for this. From the fifty-nine million cubic metres of hydrogen, about twenty thousand tons of nitrogen are fixed in the ammonia factory, so that the value for the total products is obtained which you see in the slide.

From these figures can be seen, that the value of the products may, by the addition of a nitrogen factory, be almost doubled in comparison with the value derived from coking and by-products alone, whereas, a mine which simply sells its coal, only produces products, which are two-fifths of the possible value, if a nitrogen factory is attached.

The above figures for the increase in the value of the product by using the coke oven gas, can only be properly appreciated in the light of the cost of the new factory. The proportion of the increase in capital cost and the increase in the value of the products is summarized in the following statement.

From this it will be seen, that the increase in the capital cost of the plant, compared with the increase in the value of the process, is relatively small.

I usually do not give the working expenses for our method in figures, as they vary with regards to power, gas, wages and so on, according to the different countries. The cost can easily be calculated by giving you the number of kilowatt hours required, the amount of cubic metres of gas consumed and the number of workmen employed. These figures are shown in the following table.

The conversion into ammonium sulphate requires about five kilograms of sulphuric acid per kilogram of nitrogen, which amounts to about twenty-one pfennig per kilogram of nitrogen in Germany to-day, figuring a price of four marks and twenty pfennig per one hundred kilograms of sulphuric acid. To this is added from two to three pfennig for the working cost. The conversion into nitrate, however, is much cheaper.

The Mont-Cenis process was developed during the years of 1925 and 1926. It was first tested in the laboratory and then was put

into practice at a trial plant with a capacity of about three thousand tons of nitrogen per year.

As a result of these experiences, the Gasverarbeitungsgesellschaft, near the coking plant of the Gewerkschaft Mont-Cenis in Herne-Sodingen, built the first large plant with a capacity of about eighteen

TABLE V

REQUIREMENTS FOR A PLANT IN CONNECTION WITH THE MONT-CENIS PROCESS,  
WITH A CAPACITY OF ABOUT 30,000 T PER YEAR UNDER  
GERMAN CONDITIONS

12 ha land for the proposed plant, including conversion of nitrogen to ammonia  
150,000 cbm = 5,308,140 cubic feet enclosed space for factory buildings, comprising buildings for:

	CUBIC METERS	CUBIC FEET
Compressors and separation plant.....	85,500	3,019,600
Engines for synthesis.....	18,200	642,768
Synthetic furnaces.....	19,000	671,022
Cooling tower.....	8,100	286,077
Workshop.....	11,000	388,486
Laboratory.....	8,500	300,194
	150,300	5,308,147

The plant for the conversion of nitrogen to sulphate and nitrate requires:

For sulphate plant.....	24,000	847,607
For oxydation plant.....	5,700	201,307
For nitrate plant.....	17,700	625,110
For engine house.....	900	31,785
	48,300	1,705,809

The process requires for each kilogram of nitrogen in ammonia (at a percentage of hydrogen of 48-50 in coke oven gas):

$3\frac{1}{3}$  kilowatt hours

7500 German calories = about 30,000 B.t.u. in form of coke oven gas.

150 workmen

$\frac{1}{3}$  of the amount for wages is added for salaries

5.5 Pfennig for chemicals, raw materials and repairs.

thousand tons in connection with its coking plant. It is in full working order now and has proved very satisfactory. A second plant, with a capacity of over twenty thousand tons of nitrogen is now under construction in connection with the coking plant of the fiscal mine Hibernia. The Prussian government has taken great

interest in these two plants and in fact, is part owner through the Hibernia.

We have also succeeded in interesting people in foreign countries in this method. Our plant too is starting production soon.

#### DISCUSSION

DR. H. A. CURTIS: I think we should not fool ourselves with reference to the situation of Chilean nitrate. Mr. Battig gives the impression that Chilean is done for, even taking into account the variation of the process, as he calls it.

You must remember that the old Shank's process was put in something like fifty years ago in Chile, and because there was no incentive to make very large improvements in that process, the industry was at least forty years behind the times when the final competition between synthetic products and Chilean nitrate developed in the last few years.

The Guggenheim plant built down there has been successful in its operation, as we understand, and if there is anything in the claims they make, there has been a great saving, at least in the technical side of preparing Chilean nitrate, which saving is to be reflected in lowered cost of nitrate. It seems to me that if the first real attempt to make a large improvement in the industry can result in any such cheapening as the Guggenheims claim, it is fair to assume that there will be improvements made in the Chilean nitrate industry which will put it in a very much better position to compete. I think we are going to have Chilean nitrate on the market for a long time.

# THE PROCESSES OF GEORGES CLAUDE FOR THE SEPARATION OF GAS BY LIQUEFACTION AND THE SYNTHESIS OF AMMONIA

By JEAN DELORME

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The processes for separating the gases contained in gaseous mixtures through their partial or total liquefaction constitute a technique which is and should be widely utilized in the industrial progress which turns now towards an ever more complete and more rational use of the natural richness of the soil, and especially of the solid fuels. The present treatment of these fuels generally produces a gaseous mixture containing very different components which, though not fit to be used rationally when aggregated, might, when separated, be adapted by means of processes already industrialized, or likely soon to reach this stage, to the most pressing requirements of the industry.

## APPEARANCE OF CHEMICAL PROCESSES

A first step was realized by means of chemical processes in connection with the high temperature distillation of coal; it soon appeared irrational to leave ammonia in the heating gases and ammonium sulphate was manufactured out of it. Further, the solid and liquid hydrocarbides which could find a better use than being consumed for heating ovens, were extracted.

Later on it was thought that a more important separation might follow this first process and that it would be interesting to extract the hydrogen from the coke oven gas.

## EXTENSION OF SAME TO HYDROGEN PRODUCTION

As a matter of fact, the hydrogen requirements were soon acutely felt: its use confined to aeronautics soon extended to the chemical industry through its use for hydrogenation of oils and coals and manufacture of synthetic ammonia fertilizers and fuels.

Foreseeing that there would be some day a hydrogen problem, Mr. G. Claude had already indicated in 1903 how to apply to the separation of hydrogen from gaseous mixtures, the principles which

enabled him to realize the separation of air into its components. On the other hand, shortly before the war, Professor Linde began to work out the same question. But a remarkable property of hydrogen prevented at first the success of his experiments: While all gases cool through expansion by simple discharge, hydrogen warms at all temperatures above  $140^{\circ}\text{C}$ . ( $284^{\circ}\text{F}$ .), therefore, it could not be relied upon for the production of cold.

Professor Linde was very clever in removing this drawback, as he connected to his hydrogen apparatus an auxiliary circulation of nitrogen, this gas cooling by expansion.

It is only after the war that Mr. Claude, extending the results obtained in 1903 and already mentioned as fit to be applied to more complex gases such as coke oven gas, undertook a series of most remarkable tests and experiments at the Air Liquide Company and carried them out by the Societe Chimique de la Grande Paroisse, in order to solve the problem of separation of the gases contained in the gaseous mixtures produced by the high temperature distillation of coal.

#### APPLICATION OF LIQUEFACTION PROCESSES TO COKE OVEN GAS

Let us now examine the application of these liquefaction processes to the treatment of coke oven gases.

##### *1. Hydrogen and ammonia synthesis*

*a. Hydrogen.* You know how complex these gases are; you know that apart from their main components—hydrogen, methane, nitrogen, carbon monoxide, they contain a whole series of carbides;—ethylene, propylene, acetylene, benzol, the liquefaction and solidification points of which range from room temperature to minus  $170^{\circ}\text{C}$ . In order to eliminate the most heavy carbides M. Claude utilizes the pressure scrubbing of benzol with heavy oil. The gas thus purified enters two heat exchangers where it is cooled by the cold exit gases; during this cooling the last trace of benzol and steam disappear and the light carbides condense. As they condense, the impurities are gradually collected and drawn out of the exchanger. The coke oven gas, reduced to its major constituent then reaches the so-called separator.

In this apparatus occur two liquefying stages; the first where methane condenses, the second where carbon monoxide and a part

of the nitrogen condense. The remaining gases then circulate through the upper part of the apparatus where they are submitted to still lower temperature, under whose action nearly all remaining carbon monoxide liquefies, so that only compressed and very cold hydrogen leaves the separator. This hydrogen is further cooled by expansion through an engine with production of external work, and is then circulated around the upper part of the separator to produce the very low temperature we just mentioned.

This process whose simplicity is difficult to reach, does not give absolutely pure hydrogen; there remains about 0.5 per cent of carbon monoxide, a poison for the intended synthesis of ammonia, but the reaction of  $H_2$  on CO easily destroys carbon monoxide by catalysis under a pressure of 1000 atmospheres, obtaining harmless methane and water, and thus are wonderfully combined together the processes of separation of hydrogen and synthesis of ammonia.

Analysis showed that no trace of carbon monoxide remained in the gases entering the synthesis tubes.

Further, the produced hydrogen presents a most important feature; it is purified, completely free of sulphur and not only of hydrogen sulphide, harmful for ammonia synthesis, but also from organic sulphur compounds (carbon sulphide and oxysulphide, mercaptans) generally present in the coke oven gas and of which the usual purification methods do not allow the elimination.

Before we proceed, let us mention that pure hydrogen might be obtained with the same apparatus through injecting, under liquid form, a part of the less condensable component which then acts as a scrubber. The scrubbing liquid therefore used is to be less volatile than the carbon monoxide itself; the only one meeting these requirements is nitrogen. As a matter of fact, apparatus where hydrogen is scrubbed by liquid nitrogen is already in use and it is only necessary to adapt a nitrogen scrubbing tower to a Claude apparatus to easily obtain pure hydrogen. The hydrogen apparatus above described is now readily used; the existing units realized by the "l'air liquide" are able to handle respectively 1.500 (52,950 cubic feet) 3.000 (105,900 cubic feet) or 6.000 (211,800 cubic feet) cubic meters of coke oven gas per hour.

Liquefying units using G. Claude Process in operation, one being erected, represent actually a total capacity corresponding to an actual production of more than 450 tons (900,000 pounds) of ammonia per day. Twelve of these are of the 6000 cubic meters (211,800 cubic

feet) of gas per hour type. In Belgium, for instance, the Claude processes were the first to be used in the manufacture of hydrogen through liquefaction. The Ougrée Works who liquefy coke oven gas by our processes in their Claude synthetic ammonia plant, have a daily production corresponding to 60 tons of ammonia. Important extensions are still considered. This industrial equipment is nearly as simple as the nitrogen apparatus of which the principle is the same and which has been used on a large scale for many years, namely for cyanamide production.

Claude apparatus able to produce more than 80,000 cubic meters (2,824,000 cubic feet) of nitrogen per hour has been installed, of which 50 per cent are produced in the United States. The biggest single unit has an output of 2.425 m<sup>3</sup> (85,602 cubic feet) of nitrogen per hour. Improved apparatus will shortly allow even a greater output.

*Synthesis of ammonia.* After having considered the application of the coke oven gas liquefaction process, i.e., extraction of hydrogen contained in this gas, let us now briefly contemplate the main purpose of this operation—the ammonia synthesis.

I cannot do better than quote a very remarkable paper of Mr. Camille Matignon, a member of the Institute of France, who wrote in "Chimie & Industrie" in August 1928:

Mr. Matignon said in part: "The ammonia processes may be divided into two great classes; the low pressure processes deriving from Haber's process, where low pressure means pressures of about 200 atmospheres and the high pressure (i.e., about 1000 atmospheres) processes deriving from Claude's process."

"Until now, the general belief was that high pressure is fit for small plants and low pressure for big plants."

"First of all, it is now industrially proved that high pressure operates as regularly as low pressure, a first advantage being that it needs simpler apparatus and thus a lower investment. A second advantage is the possibility of largely increasing the maximum capacity of the synthesis units."

In confirmation of these words on the regularity of the running of the high pressure machine, I can say that for several months machines have been operated 98% of the possible time.

Further, Mr. Matignon concludes: "It has been objected to high pressure processes that they lead to a higher consumption of electric power per kg. of ammonia. This might *apparently* seem true, but

in fact, the consumption of electric power is less with high pressure than with low pressure processes as shown by following calculation."

I will not reproduce here the calculations which bring Mr. Camille Matignon to this conclusion. I will only indicate that the economies which compensate the increased amount of energy necessary to obtain the hyper pressure come from the increase of the combination factor; from the fact that the ammonia comes out of the separators in the liquid anhydrous form and by a simple draw off.

After a very interesting general consideration of the different ways of using the hyper pressures Mr. Camille Matignon concludes again:

"When considering very large units 50/100 tons per day (100,000 to 200,000 pounds) for instance, this superiority of the units composed of several tubes becomes considerable. We had the opportunity to see a 4 stage synthesis Claude unit capable of producing 30 tons per day under 900 atmospheres. The external diameter of the largest of these tubes was not over 70 cm. (27.5 inches) and their height not over 3.50 M. (11½ feet). With an external diameter of 1 m. (39.37 inches) and 1.20 m. (47.24 inches). Outputs of respectively 50 and 100 tons (100,000 and 200,000 pounds) per day may be reached. This figure shows how easily the catalysis in tubes connected in series makes it possible to realize considerable output.

"Moreover, the use of tubes connected in series greatly regulates the output as the wearing out of the catalyst in the first tube where it is specially submitted to sudden or slow poisoning through the impurities remaining in the mixture  $N + H_3$  is automatically compensated. Gradually as the first stage catalyst wears out reducing the production in the first tubes, the following stages receive a greater amount of gas to handle, so that the total output nearly remains the same. Supposing for instance that the reduction of the first stage's output of a 4 stages synthesis unit to be 25 per cent which is quite considerable, the output of the other stages automatically increases, so that the total loss does not amount to 2 per cent and this without the necessity of any regulation of the pressure."

Looking then at the practical considerations the author says that due to the importance of the depreciation rate which characterize this industry, the principal element of synthetic ammonia cost price consists of the regularity of operations of a plant or its coefficient of practical utilization, that is to say, the ratio between the effectively realized production during a 100 days operation without

calling in spare apparatus and the maximum production theoretically possible during the same period; and Mr. Matignon concludes that any synthetic ammonia process must be able to guarantee on the hydrogen ammonia group a coefficient of practical utilization of at least 85 per cent

I will only add that in order to obtain such results it is necessary for the different parts of the plant to be perfectly adapted to each other. Mr. Claude realized this adaptation to his process for the separation of hydrogen by liquefaction and for ammonia synthesis, so as to constitute a whole. In a plant connected with a northern French mine and using the Claude processes, the coefficient of practical availability for apparatus having been operated nearly two years without any spare has been higher than 90 per cent for the hydrogen ammonia group.

b. Products of the Manufacture of Synthetic Ammonia from Coke Oven Gas. You have been in a position to appreciate, through what I have just said and quoted, that the described apparatus are now of current use, and are operated with great regularity in all plants producing synthetic ammonia by Claude's process.

It is thus possible to obtain—first a gas of high hydrogen content with some carbon monoxide and nitrogen and on the other hand residual gases containing other gaseous components, some of which can be separated. These processes, therefore, constitute a most powerful means of increasing the value of the gas.

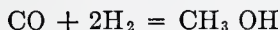
The ethylene which was diluted in the coke oven gas is concentrated in the apparatus for hydrogen production in a mixture with a high proportion of ethylene which can be used for the manufacture of ethyl alcohol.

The uses of ethylene thus obtained may be numerous, for instance in the manufacture of anti-freeze or solvents.

Methane will be very soon promoted to the dignity of raw material for the chemical industry; it may be considerably increased in value in the near future. Thanks to the liquefaction apparatus, it will probably be obtained in the necessary state of purity for further utilization, especially for oxidation and conversion to unsaturated hydrocarbons which are considered, on account of their reacting disposition, as the raw material for synthetic fuel.

Carbon monoxide, which had been hitherto considered as a catalyst poison and carefully eliminated from the hydrogen used in ammonia synthesis, may even be considered as a valuable raw material.

Through a catalytic reaction with hydrogen, it leads, for instance, to methyl alcohol according to formula:



This reaction takes place at very high pressure and under conditions similar to the reaction of ammonia synthesis, so that it has been thought advisable to combine both productions.

The American Society Lazote and The Compagnie de Mines de Bethune, both operating the Claude processes, have realized a cycle working as follows:

The apparatus for separation through liquefaction are controlled so as to leave in the hydrogen produced a proportion of about 5 per cent carbon monoxide; after addition of proper quantity of nitrogen the gas is compressed to 1000 atmospheres and submitted to a first catalysis during which nearly all the carbon monoxide reacts to give methyl alcohol which condenses immediately and at the same pressure the gas is submitted to the usual catalytic purification so that the only remaining components, hydrogen and nitrogen, are ready to combine to yield ammonia.

The proportion of the quantities of methyl alcohol and ammonia produced can be modified, according to the market requirements, by a judicious choice of the carbon monoxide proportion in the initial gas.

Lastly, the nitrogen contained in the coke oven gas naturally finds its use; it is collected as far as possible at the same time as hydrogen, so as to reduce the amount to be produced in order to obtain the necessary mixture of one part nitrogen and three parts hydrogen by volume for ammonia synthesis.

We have thus briefly looked over from the technical standpoint the field of applications for the liquefaction processes of coke oven gas. Naturally, consideration must be given in each case to the economics of the use of coke gas.

In order to try to complete this statement, before concluding I must say something on the important part that these processes may still play in the fields of the low temperature distillation. Through a new technique, the experimentors seem to endeavor to produce from the poorest fuel the most useful and paying products without destroying them by a too rough pyrogenic treatment.

But it is necessary to draw your attention to the advantage and the simplicity of the processes of liquefaction when applied to the

separation of the components of the produced gases and to obtain separately the different hydrocarbons which they obtain.

A gas containing per cubic meter:

130 grams of spirits  
7-8 per cent of ethylene  
55 per cent of  $\text{CH}_4$   
6 per cent of CO  
15 per cent of  $\text{H}_2$

and obtained by distillation at low temperature (100 m. 3 per ton of coal) could probably be treated by liquefaction. Under very low pressure, on the one hand, the spirits could be separated in different parts of varying densities, and on the other, would appear nearly pure ethylene and methane particularly convenient for the different syntheses.

The residual gas obtained which might be mixed with water gas obtained by gasification of semi-coke and composed of  $\text{H}_2$ , CO and N, free of sulphurous compounds, could after readjustment, be used for synthesis such as the ammonia and methyl-alcohol synthesis.

The water gas could eventually be used for the production of methyl alcohol, but its treatment in liquefaction apparatus similar to those in which is treated at present the normal water gas, would give pure hydrogen for ammonia manufacture and for different syntheses which might be realized for the valorization of tars produced during the low temperature distillation.

Naturally the gas can also be used for the combined production of methyl alcohol and of ammonia; it is also evident that some part of the gases would have to be used for the heating of the ovens.

I know some difficulties are still to be solved concerning the semi-coke, but simultaneous utilization of oxygen and steam, as C. Claude had tested it already in 1903, will perhaps make possible a simple solution to this problem already nearly solved.

I have showed how large the field of application of the processes of liquefaction of gases is. These allow in a general way bringing together the most important branches of modern industrial activity. By the ammonia synthesis from hydrogen, separated from coke oven gas, the producers of solid fuels are interested in the nitrogenous fertilizer industry. Perhaps we shall see, in the very near future, a new chemical industry, based on the use of coal involving the production of solvents for the dyeing of materials and artificial silk and perhaps in close connection with the transportation industry, by the production of synthetic fuels.

# A NEW METHOD FOR THE DETERMINATION OF MELTING PROCESSES IN ASH

By DR. KARL BUNTE

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The progress in furnace and gasification technology, the better design of the chain grate and of the rotating-grate-gas-producers, increase the importance of ash substance in judging the value of a solid fuel. It has been recognized more and more, and emphasized in design, that the grate is not only the carrier of the fuel, but it must also guarantee a uniform and efficient distribution of the air or steam supplied for combustion or gasification. The efficiency of this distribution of the air, or of the steam in case of the water gas process, depends, however, decisively on the behavior of the ash, or, as the case may be, on the clinkers that are formed from it. In some cases, which are by no means rare, the difficulties caused by clinkering, exclude the use of certain coals, which would appear very suitable, considering the properties of the moisture-and-ash-free fuel and the amount of ash.

Since the beginning of the century,<sup>1</sup> fuel technologists have tried to obtain as thorough as possible a knowledge of the behavior of ash and the formation of clinkers, and in most recent times this knowledge is especially demanded.

Investigating ash in respect to its fusibility, we have obtained in advance a thoroughly clear idea of the following three fundamental principles:

First: Ash is not homogeneous. It is composed of:

- a. Ash ingredients, rich in alkalis, which by genesis are a part of the vegetable matter from which coal originated,
- b. Deposited ingredients consisting, for the most part, of calcareous, silicious, and argillaceous substances,
- c. Infiltrated ash constituents, that is, carbonates, sulphates, and bisulphide of iron,
- d. Stony material.

These four kinds of ash may have a completely different character, and it is not self-evident, a priori, that the behavior of ash is characteristic for a certain coal, a coal bed or even a coal district.

<sup>1</sup> Le Chatelier, *Bulletin Soc. d'encouragement*, 1902, p. 273.

In fact, Sinnat, Owless and Simpkins<sup>2</sup> were able to show that the genetic ingredients of coal, fusain, durain, and clarain give different kinds of ash whose melting points lie between 1,200° and 1,450°. The amount of this coal-substance-ash is, however, so small in comparison to the amount of ash technically present that these differences are of small importance. Nevertheless, their effects have been shown in the somewhat different melting points of the ash with different sizes of grain, depending upon the content of fusain.

The behavior of the ash of coal which is free of stony material is caused principally by the infiltrated ash; and that of mine-run-coal depends still more on the mineral ore carried along. These are defined so well geologically that Constam<sup>3</sup> was able to determine that the ash melting point is in certain limits an index of the mineral substance of a definite bed of coal. Fieldner has even shown that the ash melting point, within certain limits, is characteristic of certain American coal districts; and in Germany, certain coal districts and coal species are known, which have quite generally shown themselves favorable or unfavorable with respect to the behavior of the ash. The behavior of ash may then be regarded as characteristic at least for a specific coal or coal bed in spite of the fact that the four kinds of ash are depending on circumstances represented to a different degree.

The second point is the following:

If one looks at what remains of the coal after careful combustion (Fig. 1), there can be recognized stones and slate, on the one hand, and the dispersed ash on the other hand, each lying separate. With a microscope we see that even in the ashy skeleton of the pieces of coal or coke the original structure is well maintained, and also that in the ash of pulverized coal certain constituents can be clearly recognized (Fig. 2). The individual constituents, namely, stones, gypsum or lime as a crystalline crack filler, and iron pyrites from the infiltrated ash, do not lie absolutely in close proximity. In every method of the preparation of test-samples, however, the ash is ground finely and thoroughly mixed, so that the probability is many times increased that the individual ash constituents can influence each other to a large extent in comparison to technical firing. One must clearly understand this deviation from practical behavior even if it cannot be changed.

The third point is this:

<sup>2</sup> *Journ. f. Gasbeleuchtung*, 1913, p. 1161.

<sup>3</sup> *Journ. Soc. Chem. Ind.*, 1923, p. 266.

The melting process varies depending upon the state of oxidation of the metals in the ash, especially of the iron in it. Fieldner<sup>4</sup> has shown this in detail, and pointed to the fact that the surrounding atmosphere exerts considerable influence. The atmosphere in experiments must be as similar as possible to that of the technical ash melting zone. It will not be far from right, to assume, substantially, an atmosphere in which the equilibrium of gases corresponding to the



FIG. 1. REMAINS OF COAL AFTER COMBUSTION

temperature, has been established. Such an atmosphere is supplied, for example, by a granular-carbon-resistance-furnace if it has not been artificially disturbed by the introduction of gases.

On account of the nature of the ashes, we never encounter, in the formation of clinkers, a well-defined fusion point as in the case of homogeneous chemical substances. There takes place, on the contrary, a more or less rapidly occurring softening process. Almost

<sup>4</sup> *Fuel*, 5 (1926), p. 24 ff.

all observers who have tried by different methods to investigate the behavior of the ash in the fire, have sought to distinguish between a softening point and a fusion point, or even also a liquid point.

In the most commonly used method, that of cones, the so-called cone fusion point represents no definite temperature indication; it represents, accurately speaking, that temperature which has been reached after a uniform increase in temperature, when the mass that has already become plastic, has collapsed to a certain degree on account of its own dead weight.

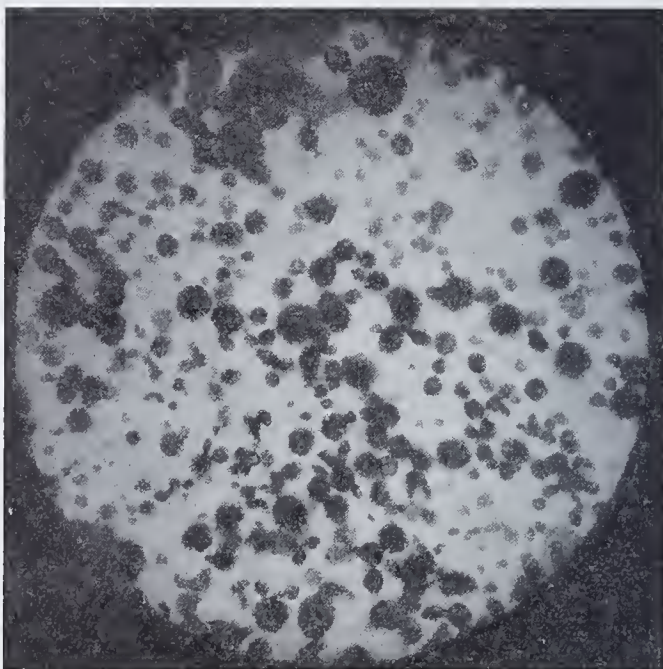


FIG. 2. MICROSCOPIC VIEW—ASH FROM PULVERIZED COAL

In the Gas Institute at Karlsruhe we now use for the characterization of the fusibility of an ash, a method concerning which I made a report some time ago in collaboration with Dipl. Ing. Baum, which permits us to follow by measurements, the whole process of softening. It corresponds to the requirements of (a) objective observation, of (b) an atmosphere that is in oxidation equilibrium, of (c) accurate reproducibility to a few degrees. It results in characteristic fusion curves which give a new and surprising insight into the melting process and it permits valuable deductions as to the nature of the melt-

ing process and of the behavior of the ash constituents. This method has been favorably received.

We use an electrical granular carbon resistance furnace (Fig. 3) with a vertical heating tube 60 mm. in diameter and closed at the bottom; a cylindrical sample of 25 mm. in diameter and height was put on a block of electrode carbon. By means of a rheostat the temperature is regulated in such a way, that it rises to 800°C. in

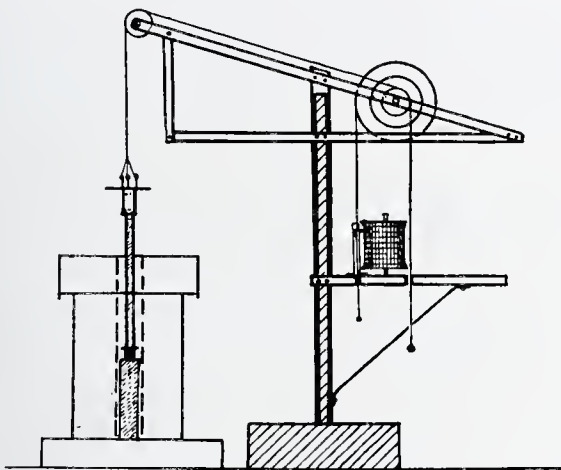


FIG. 3. ELECTRICAL GRANULAR CARBON RESISTANCE FURNACE



FIG. 4. COAL SAMPLE BEFORE AND AFTER MELTING

about one hour, and from then on, 5° per minute or 25° per 5 minutes. On the sample is a small carbon plate and on this the perforated upper bar which is 50 cm. long and 30 mm. thick. This bar is also of electrode carbon and is equipped with a suspension and motion transmitting device by means of two ball bearing rollers. Its sole purpose is to establish contact with the sample during the melting process, in order to register immediately every change of form like a sort of feeler. The thermo element is introduced through the per-

formation and rests on the middle of the sample.<sup>5</sup> The downward motion of the upper bar which is caused by collapsing of the sample, is recorded in a fourfold enlargement on a drum which makes one revolution in 3 hours. So the course of the softening and melting is automatically recorded until the sample is reduced in size to a layer of 7 mm. thick (Fig. 4). In the meanwhile vitrification has set in. In this way the subjective opinion of the observer is eliminated because he has to look only after the increase in temperature. The latter could also be automatically regulated and recorded. More particular details, as experiments on the influence of the increase in temperature, uniformity and duration of the influence of heat, re-

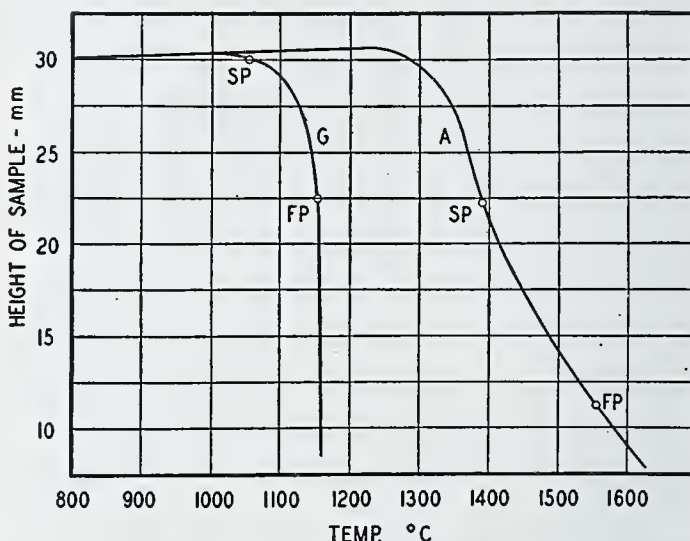


FIG. 5. BEHAVIOR OF HOMOGENEOUS ASH

producibility, etc. showed the serviceability of the experiment. Fusion curves obtained according to this method can be divided into three groups, which characterize, in each case, fundamentally different melting processes.

The first group (Fig. 5) represents the behavior of ash which is substantially homogeneous. They show how ash G melts with an almost definite fusion point. The collapse follows the initial softening as quickly as possible considering that the fusion temperature must penetrate to the interior of the sample. Typical softening curves may also appear as the curve of ash A, in which can be observed

<sup>5</sup> Hormuth and Veffler, Heidelberg, Germany.

a uniform but gradual change of plasticity. This curve shows incidentally another phenomenon. The waves in the curve are not to be attributed to the irregular operation of the recording device but

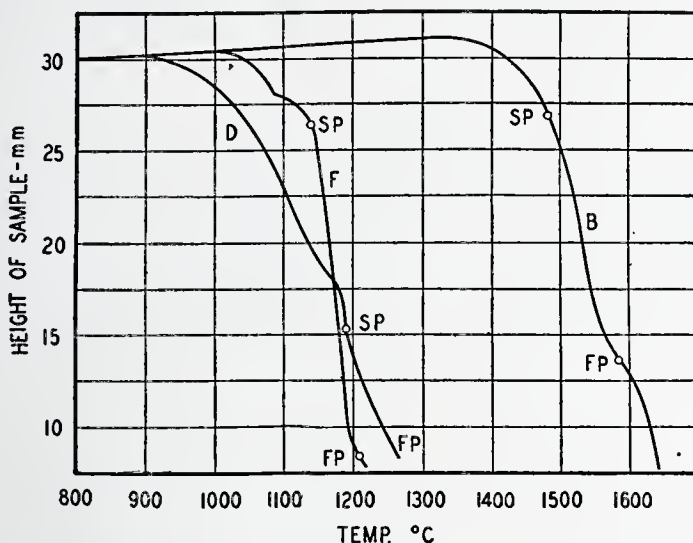


FIG. 6. BEHAVIOR OF HETEROGENEOUS ASH

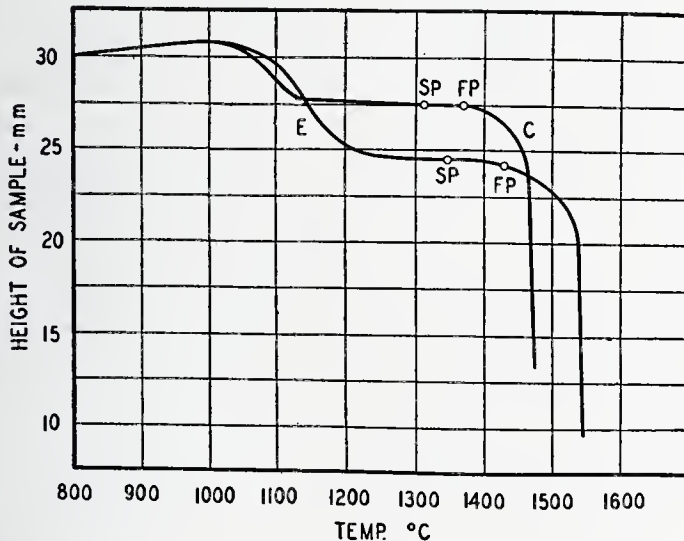


FIG. 7. SHOWING INTERRUPTED MELTING OF ASH

to the generation of gases, which in this case could be determined by the analysis of the unmelted and melted ash, to be the development of  $P_2O_5$  (content of the ash 4.0 per cent, of the clinkers, 1.1 per cent

$P_2O_5$ ). Also the vesicular structure of the molten mass proves the formation of gas.

Ash that melts quickly can be judged substantially only from the fusion temperature. It will melt rapidly and congeal rapidly, thus

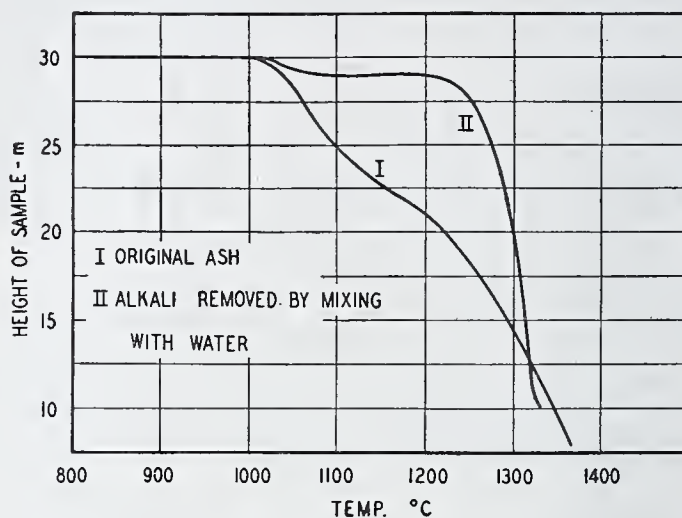


FIG. 8. EFFECT UPON ASH OF WASHING WITH WATER

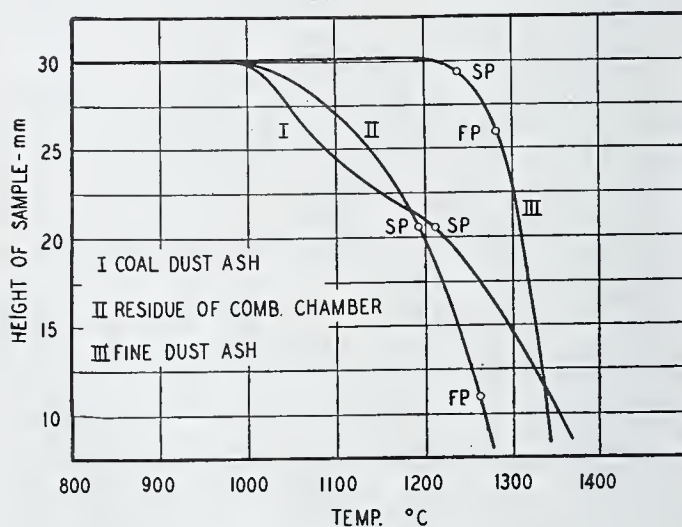


FIG. 9. ASH MELTING CURVES

yielding friable clinkers. Ash with a long period of softening must, on the other hand, lead to the much feared tough clinkers, and sometimes to stringy clinkers.

A second series of ash curves (Fig. 6) shows halting points in the fusion curve (ash D and F). These halting points which can be fully reproduced, indicate heterogeneous ash, and are explained by the third and more interesting kind of fusion curves.

With many kinds of ash we found that the melting process, which starts at a rather low temperature, stops in a thoroughly reproducible manner, and that the sample does not melt completely until it has reached an essentially higher temperature (ash C and E, Fig. 7). There are two explanations for this phenomenon. One is that one part of the ashy mixture melts at low temperature and flows out or runs into the pores between the residual constituents. The other is that the part which melted first, united with the rest to form a silicate that melted at a higher temperature.

TABLE I

CHEMICAL COMPOSITION	ORIGINAL COAL DUST ASH	RESIDUE OF COMBUSTION CHAMBER	FLUE DUST ASH BEHIND ECONOMIZER
SiO <sub>2</sub> .....	16.40	20.4	19.35
Al <sub>2</sub> O <sub>3</sub> .....	16.75	16.5	15.10
Fe <sub>2</sub> O <sub>3</sub> .....	20.40	28.9	24.80
CaO.....	22.65	20.9	27.35
SO <sub>3</sub> .....	20.19	4.5	5.07
M <sub>2</sub> O.....	4.02	4.9	4.62
Alkalines.....	2.19	6.9	6.71
Total.....	100.00	100.0	100.00
Softening point.....	1,200	1,180	1,225
Fusion point.....	1,255	1,258	1,275

Investigation of a coal ash before and after an intensive treatment with water supports the correctness of both views (Fig. 8). The originally large proportion of alkalis and alkaline earth causes an abundant formation of low melting compounds. By washing their amount is lessened and the first melting is less prominent. The fact that we have to deal here not solely with selective fusion but also with reactions and formations of new compounds, such as silicates, is evident from the depression of the final fusion temperature.

It seems to me that from these curves, it follows that it is impossible—and why it is impossible—to draw a conclusion as to the fusion point from the relation of the basic and acid constituents. The old maxim *corpora non agunt nisi fluida* is also valid here. Calcium

oxide for instance (from  $\text{CaCO}_3$ ), aluminum oxide ( $\text{Al}_2\text{O}_3$ ) and silica are practically unmeltable in the furnace. Their mechanical mixtures behave in the same way until a faster melting constituent dissolves them. The calcium aluminum silicates (e.g., clay garnet) on the contrary, which can have the same analytical composition, melt easily.

The insufficiency of such a calculation of the melting properties can be shown also in practical examples (Fig. 9). I select the melting curves of ashes from a powdered coal furnace, which very approximately show the same proportions.

I is the ash of the powdered fuel,

II is the ash from the combustion chamber,

III is the ash from flue dust pocket.

Curve I shows by its flattening between 1,100 and 1,200°C., that substantially two ash ingredients occur, one that melts easily, and the other one that melts with difficulty. The softening in the cone is not noticed until the beginning of the melting of the second constituent. In the combustion of powdered coal the two seem to have separated.

The cone fusion points with 1,270, 1,250, and 1,275 do not show any considerable differences at all, also the softening points at the cone do not lie very far apart with 1,210, 1,180, and 1,255. The temperatures observed as softening points characterize, above all, for I and II a wholly different softening condition than for III.

I believe that just this example shows quite clearly that the method of determining the ash melting curve is suitable for giving a more conclusive picture concerning the behavior of ash in the furnace than hitherto existing methods. I feel sure that this advantage will compensate for the only disadvantage which I do not want to pass by unmentioned; namely, that one needs a considerably greater amount of ash for the investigation than in the cone or rod method.

Observations of the behavior of the ash investigated in practice have so far agreed well with the conclusions relative to the kind of fusion which we drew from the curves.

We are occupied in getting the curves of well-known mixtures of minerals as pure as possible; clay, silica, gypsum, iron pyrites, fayalite, and others; to also obtain, if possible, information about the causes of the forms of the individual curves.

## REMOVAL OF ASH AND LOSS OF CARBON FROM BOILER FURNACES

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All coal has ash which remains as a residue after the combustible matter is burned. The problem of burning coal consists not only in obtaining complete and efficient combustion, but is also one of removing the ash from the furnace with little or no disturbance of the combustion process and at the least expense. There should never be an accumulation of ash or clinker which requires taking the boiler out of service for its removal, and preferably no reduction in capacity or efficiency during intermittent ash removal periods.

Ash is removed from a furnace either through the ash pit or is carried away by the flue gases in the form of flue dust. Some fuel or carbon is invariably removed with the ash, and this should obviously be kept at a minimum.

### HAND FIRED FURNACES

Hand fired furnaces with stationary grates are limited in many ways, and one serious disadvantage is the accumulation of ash and the fusing of it into clinker on the grates. This condition chokes the air supply and requires intermittent removal, and heavy manual labor, with reduced capacity and efficiency during the cleaning period. The amount of carbon loss depends a great deal upon the care of the fireman.

Flat shaking or rocking grates enable the fireman to remove ash more frequently with less labor, provided the ash does not have a fusing temperature sufficiently low to cause clinkers. The carbon loss is likely to be even higher than from stationary grates, depending largely upon the skill and care of the fireman.

### MECHANICAL STOKERS

Stokers with dump grates have been used extensively. The dump grate is usually at the bottom of an inclined grate of either the over-

feed or underfeed type. The operation of the stoker proper is not seriously interfered with when the dump grate is cleared at intervals as needed. The concentration of ash and clinker on the dump grate is likely to form larger clinkers which will bridge the dump and adhere to the bridge wall, requiring much manual labor at dumping periods.

Clinker grinders have been used in one form or another for many years. The earlier designs were applied to the middle of the furnace with inclined-grate side-feed stokers. The grinding elements were relatively light and close to the active fuel bed and some coke was removed with the ash and small clinkers, while larger clinkers bridged over the grinding rolls and required removal by hand.

Clinker grinders of very rugged construction are now extensively used as the means of removing ash and clinker from underfeed retort stokers. This is accomplished very effectively, and only occasionally, provided the surrounding furnace walls have been properly water cooled to prevent clinker ledges, does the pit above the clinker grinder bridge over so as to require manual labor for ash removal. By making the volume of the pit above the clinker grinder large enough to retain the refuse until the coke is well burned out, the carbon lost through the clinker grinder is kept satisfactorily small.

Traveling or chain grate stokers provide a simple and effective means of ash removal from furnaces. The earlier natural draft chain grates gave high losses in carbon if the grates were kept well covered or in excess air if the coke was well burned out. The modern chain grate with compartments and forced draft under control produces high rates of combustion with low carbon loss.

In the case of either hand or stoker fired furnaces clinker will adhere to the fire brick walls within the fuel bed zone, building out ledges which interfere with proper operation. Water cooled walls surrounding the fuel bed zone have done much to prevent this accumulation of ash and clinker.

#### CARBON LOSS

In Table I are presented data relating to carbon loss from coal fired furnaces which have been compiled from various sources including reports of the Prime Movers Committee of the National Electric Light Association. Most of the stoker data are taken from tests and hence should be representative of best conditions and comparable one with another. The hand fired data are likewise taken from tests on various kinds of coal.

Some of the earlier stokers gave higher carbon loss than did hand fired furnaces. The stokers had the advantage of mechanically feeding the coal. The ash was also supposed to be removed mechanically, but manual aid was usually required. Very marked improve-

TABLE I  
CARBON LOSS FROM COAL FIRED FURNACES

YEAR	METHOD OF FIRING	EQUIPMENT	FUEL	CARBON LOSS		
				Low	High	Average
				<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
1900-25	Hand	Flat grates	Bituminous and semi-bituminous	0.70	6.30	2.54
1900-25	Hand	Rocking or shaking grates	Bituminous coal	1.00	5.20	2.74
1900-25	Hand stoker		Bituminous coal	1.03	5.74	2.36
1900-25	Over feed	Front feed	Bituminous coal	3.40	5.90	5.00
1900-25	Over feed	Side feed, V type	Bituminous coal	1.86	4.08	3.00
1900-25	Chain grate	Natural draft	Bituminous coal	0.70	22.00	5.76
1900-25	Chain grate	Compartment	Bituminous coal	0.70	9.30	3.9
1900-25	Under feed	Single-retort	Bituminous coal	1.19	8.50	2.87
1900-25	Under feed	Multiple retort, dump grate	Bituminous coal	0.59	10.30	3.42
1900-25	Under feed	Clinker grinder	Bituminous and semi-bituminous	0.34	10.0	2.60
1925-27	Underfeed-retort	Clinker grinder	Bituminous and semi-bituminous	0.3	5.89	1.40
1925-27	Chain grate	Forced draft compartment	Bituminous coal	0.31	4.62	1.85
1925-28	Pulverized coal	Various	Bituminous and semi-bituminous	0.1	3.5	0.6

ments have been made in stoker design so that the latest results show a marked decrease of carbon loss as well as of excess air. The size and capacities have been greatly increased and the operating labor materially reduced.

From the various types of stokers that have entered into this de-

velopment, the two which have persisted with the best results are shown in Table I as the underfeed retort stoker, and the traveling or chain grate with compartments. Each of these has its limitations with respect to character of coal and the nature of ash in same.

The carbon loss data from hand fired furnaces and stokers in Table I include only that discharged to the ash pit. In the earlier installations with relatively low rates of combustion per square foot there was not much additional carbon loss in the form of "cinders" and flue dust, but with the high rates of combustion prevailing today the carbon carried away physically with the flue gases is an appreci-

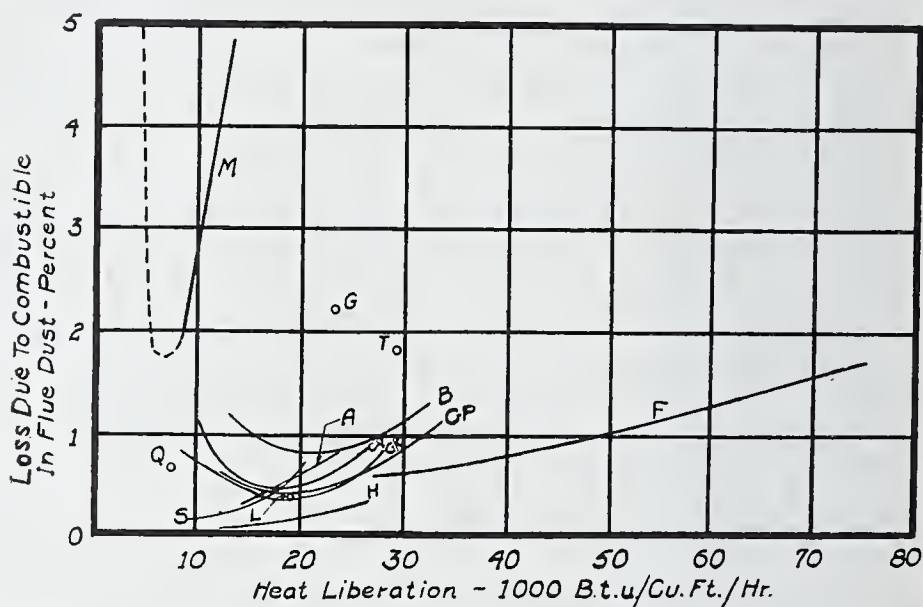


FIG. 1. EFFECT OF FURNACE LIBERATION ON THE LOSSES DUE TO COMBUSTIBLE IN FLUE DUST

able item, and should be separately determined instead of leaving it to become part of a relatively high "radiation and undetermined loss."

### PULVERIZED COAL FURNACES

In burning pulverized coal there is very little carbon lost to the ash pit. The data in Table I relating to pulverized coal consist almost entirely of carbon loss in flue dust. The removal of ash from pulverized coal fired furnaces has been accomplished more or less successfully in several different ways.

Flat bottom furnaces of brick construction from which the ash is drawn out manually as shown in Figure 22, have been used under smaller boilers and have been satisfactory only when using coals having a high fusing temperature ash, or when operating at limited ratings.

Hopper bottom furnaces without water cooling (see Figure 16) are similarly limited if trouble due to bridging and building up of fused ash and clinker is to be avoided.

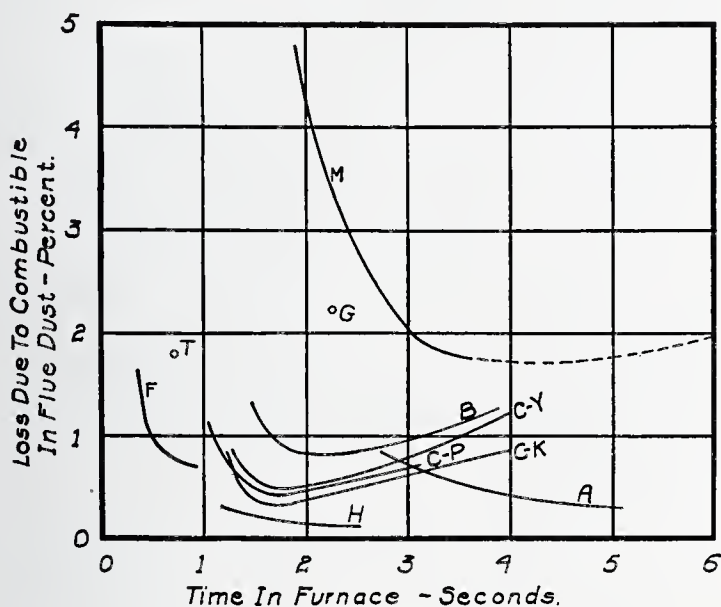


FIG. 2. EFFECT ON FLUE DUST COMBUSTIBLE LOSSES OF THE AVERAGE TIME FUEL PARTICLES REMAIN IN THE FURNACE

Water screens, consisting of water circulating tubes spaced 14 inches or more apart and located several feet above such hoppers or furnace bottoms absorb enough heat from the ash so that either higher rating or lower fusing temperature ash can be used. Even this construction has its limitations, which if exceeded will result in ash fusing and building up until its removal is very difficult.

The carbon loss through the ash pit is very low with any of the three last mentioned furnaces, as the furnace floor is hot enough to keep any coarse coal or coke smoldering should it fall to the floor. The real trouble with any of these types comes when the ash fuses and solidifies in such a manner that it bridges over the gates and

cannot be removed until the furnace is cooled down and the fused ash mined out.

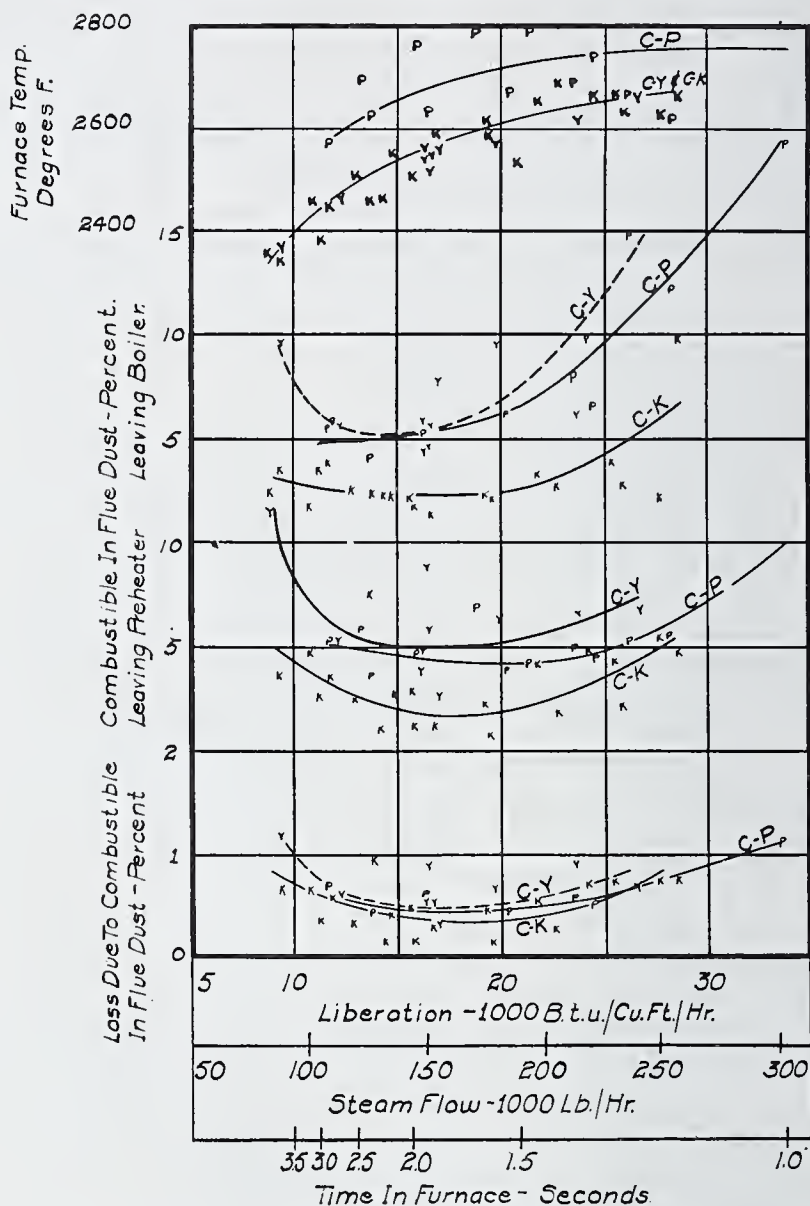


FIG. 3. DETAILED DATA SHOWING FLUE DUST COMBUSTIBLE RESULTS FROM TESTS WHEREIN THREE DIFFERENT KINDS OF COAL WERE BURNED

Furnaces with water cooled hopper construction, such as shown in Figures 18, 20 and 21, are suitable for still lower fusing point ash or

higher ratings. The ash will mostly slide down the smooth cooled iron hopper floor to the ash pit, but should the temperature become higher than the fusing point of the ash in the coal it will run down the

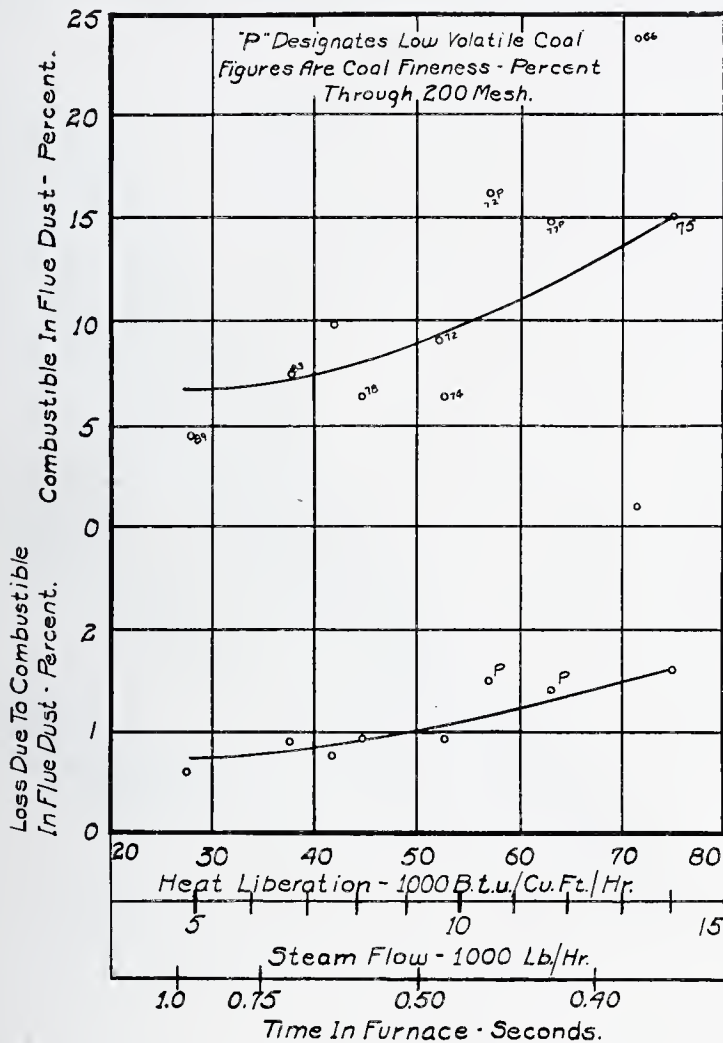


FIG. 4. FLUE DUST COMBUSTIBLE, FURNACE F

Note high furnace liberation and short time in furnace illustrating the advantages of turbulent burning in attaining low combustible loss.

hopper in a molten condition with no ill effect. The carbon loss from a water cooled hopper floor may be slightly higher due to the carbon being chilled when it rolls into the hopper, but if the coal is

properly pulverized this will not be an appreciable loss. In other words, this loss depends upon the preparation of the coal and the effectiveness of the burner rather than upon the type of furnace.

The latest and most interesting method of removing ash from a pulverized coal furnace is to tap it out in a molten condition. Such a

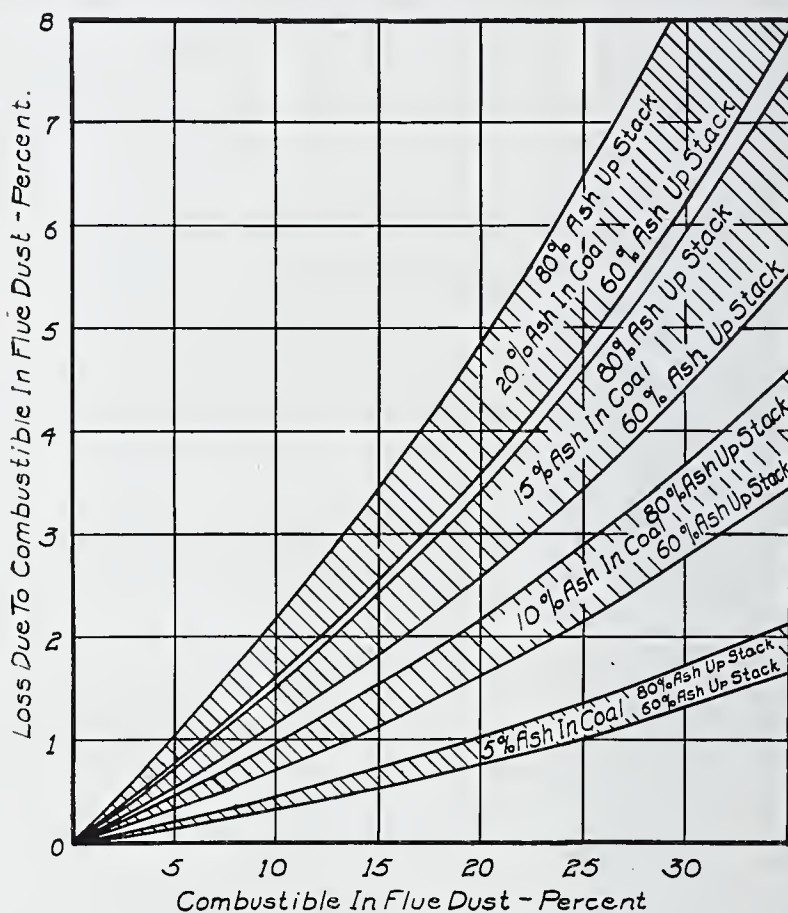


FIG. 5. VARIATION OF FLUE DUST COMBUSTIBLE LOSSES FOR COALS OF DIFFERENT ASH CONTENT AND PER CENT OF ASH UP THE STACK

furnace construction is shown in Figure 17 having protected water cooled walls on four sides. The floor is supported on a steel plate and consists of three courses of fire brick covered with dolomite or other suitable material on which the molten ash accumulates. The floor plate is properly sealed to the side walls to prevent any slag leaking through.

By locating the burners near the bottom of the furnace and properly directing the flame against the pool of molten slag which accumulates on the floor, very effective combustion is obtained. The entire accumulation of ash resulting from that which drops out of the flame, flows down the walls and drops from the boiler tubes, can be kept in a molten condition.

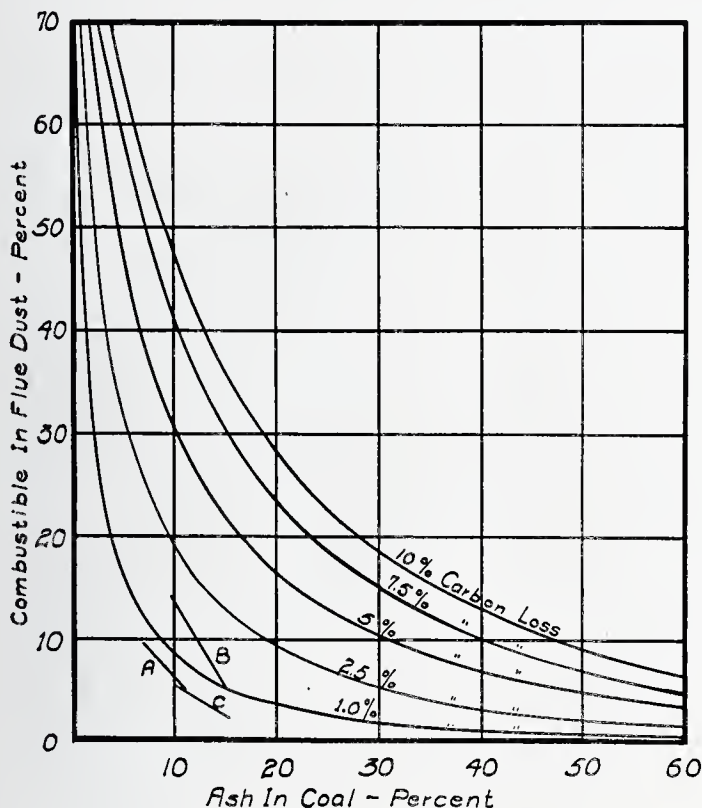


FIG. 6. EFFECT OF PER CENT ASH IN COAL ON CARBON LOSS

Curves from furnaces A, B and C show same general direction as iso-loss curves

As 20,000 to 30,000 pounds of molten slag can easily be tapped out in an hour, it is usually necessary to remove the ash only once in 24 hours. This molten ash is entirely free from carbon and is readily handled by striking the stream of slag with water jets which break it up and deliver it in granular form to a sluicing system. This system has the advantage of collecting a larger percentage of ash than if it were removed in a dry and dusty condition. It is a very clean method

as there is no dust or other nuisance around the boiler room and a minimum of labor and expense is required for the removal of ash in this manner.

Furthermore, the flue dust which is collected in different parts of the boiler passes or any other separating device can be returned to the furnace and delivered in a condition suitable for other uses. Coal

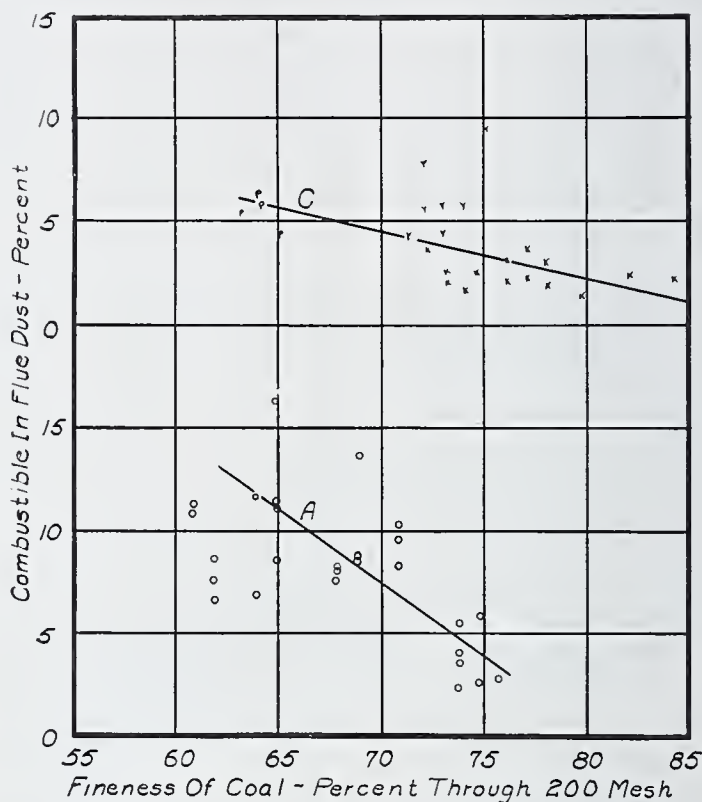


FIG. 7. EFFECT OF COAL FINENESS ON COMBUSTIBLE IN FLUE DUST SHOWN BY PLOTTING DETAILED DATA FROM FURNACES A AND C

with ash having more than 2,500°F. fusing temperature has been satisfactorily handled. It is believed that with more experience and study this system will be generally adopted and the resulting slag will be readily disposed of to advantage.

The heat loss resulting from removing this ash in a molten condition amounts to approximately one-tenth of one per cent, for the removal by this method of each 2.5 per cent of ash in the coal.

## FLUE DUST

There is some dust in the flue gases from every furnace burning coal. This dust consists of coke or fine particles of coal which naturally contain their quota of ash. There is also some ash free from carbon or coke consisting of particles from which the carbon has been

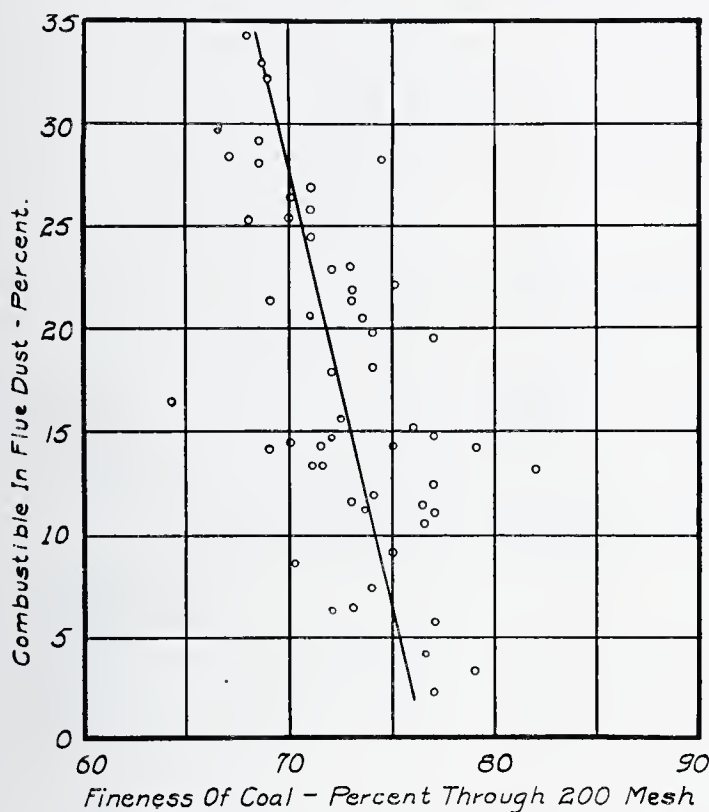


FIG. 8. EFFECT OF COAL FINENESS ON COMBUSTIBLE IN FLUE DUST.  
DETAILED DATA FROM TESTS ON FURNACE D

completely burned. There is also soot, which is precipitated carbon from hydrocarbons being improperly burned within the furnace.

Discharge of soot usually comes from hand fired furnaces or poorly operated mechanical stokers and is the basis for most of the visible smoke. This is more likely to be discharged from furnaces operating at low ratings than at higher ratings with forced draft, as under the latter condition there is more turbulence and mixing and higher temperatures within the furnace. At the higher ratings the dis-

charge of coke and ash with the flue gases is greatest, as the velocities will carry larger particles away with the gases.

The remainder of this paper will be devoted largely to a discussion of data relative to the discharge of flue dust and the factors which influence the loss of carbon from this source.

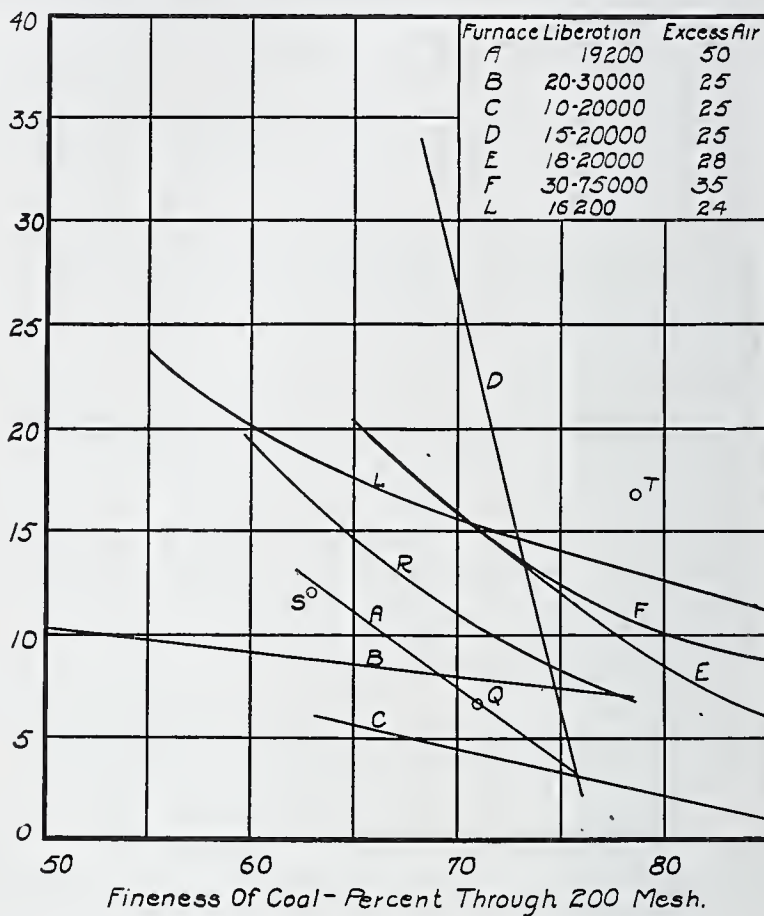


FIG. 9. EFFECT OF COAL FINENESS ON COMBUSTIBLE IN FLUE DUST, COMPOSITE CURVES

In the case of stokers or fuel bed combustion the carbon and dust loss is largely dependent upon the character of fuel and the velocities through the fuel bed. The loss is less with coking coals than with free burning coals, and with the latter the loss depends upon the fineness of coal as fired.

Flue dust discharged from fuel beds is coarser than that from pul-

verized coal, as the air passing through the fuel bed will carry particles as large as will be carried by that velocity, while with pulverized coal firing the initial preparation of the coal largely governs the size of particles which can be carried from the furnace.

In burning pulverized coal, there are several factors which govern the carbon loss, some of which are:

- Character of coal
- Fineness of pulverization
- Burner design
- Furnace temperature
- Rate of combustion
- Excess air

Figures 1 to 15 have been prepared from data bearing upon these phases of the subject. Many of these data have been collected in the regular routine of boiler tests, combustion studies, burner developments, etc., also some from reports of the Prime Movers Committee of the National Electric Light Association and other sources.

Table II gives the more important features of the boilers and furnaces from which these data have been compiled, and Figures 16 to 22 inclusive show some of the furnaces from which most of the data were taken or have some special features which are worthy of special mention.

In Figure 1 data are plotted showing relation between total heat loss due to combustible in flue dust and the heat liberation per cubic foot of furnace, while Figure 2 shows loss due to combustible in flue dust from the same furnaces but plotted to the average time which particles of fuel were in the furnace, based upon the length of flame travel and the capacities being obtained.

Figures 3 and 4 represent curves of individual furnaces *C* and *F* with all test data plotted, the former showing results with three different kinds of coal designated as *K*, *P* and *Y*.

Referring to Figures 1 and 2, the furnace *M* is shown in Figure 21. It has vertical firing, flare-type burners, air cooled refractory walls on three sides, 14 cooling tubes of 4-inch diameter on 18-inch centers in the rear wall, and a water cooled cast iron block covered hopper floor and is used exclusively for burning anthracite coal. The outstanding feature of this installation is the relatively high carbon loss with rates of combustion not exceeding 13,000 B.t.u. per cubic foot and a time in furnace of between two and three seconds. The carbon



loss increases appreciably with increased velocities, thereby indicating that the time factor is important. Temperature also plays an important part, for at lower ratings and furnace temperatures below 2,200°F., it is impossible to maintain positive ignition, and naturally the carbon loss would be very high as indicated in the dotted probable curve. The furnace temperature varies from 2,500°F. to 2,700°F. at ratings between 9,000 and 13,000 B.t.u. per cubic foot. Turbulent

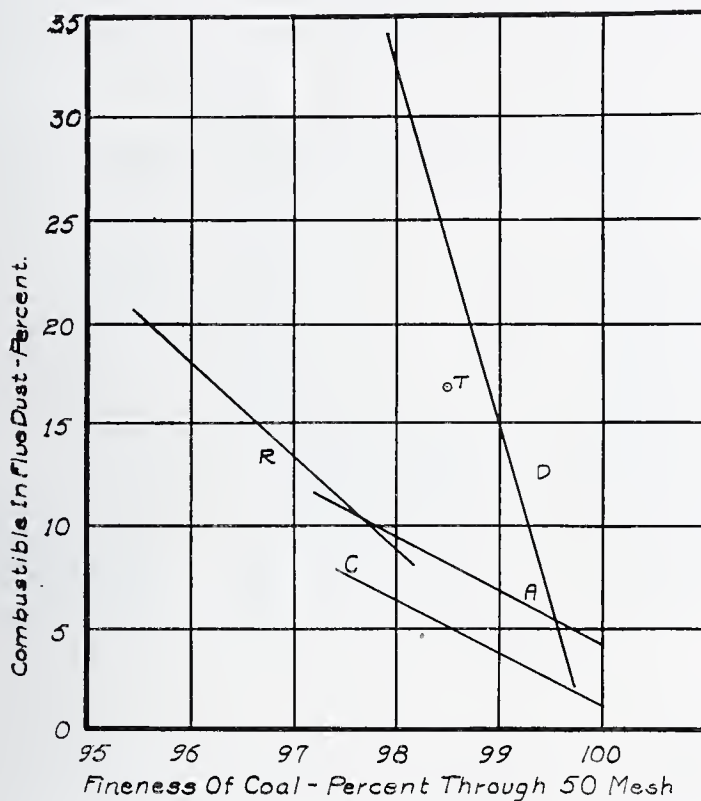


FIG. 10. EFFECT OF COAL FINENESS ON COMBUSTIBLE IN FLUE DUST, COMPOSITE CURVES

burning is not well adapted to anthracite due to the higher air velocities required being greater than the rate of flame propagation of this fuel. Fine pulverization is also essential.

Furnace G is very similar to furnace H shown in Figure 20, but is burning coal with about 18 per cent volatile. Sufficient data have not yet been obtained on this boiler, which has recently been placed in operation, to definitely decide whether the relatively higher carbon

loss is due to the low volatile coal or whether other factors enter into it, but it is believed that it is largely because of the greater amount of fixed carbon and the difficulty of burning it completely. Further improvements can no doubt be made as the subject is more carefully studied.

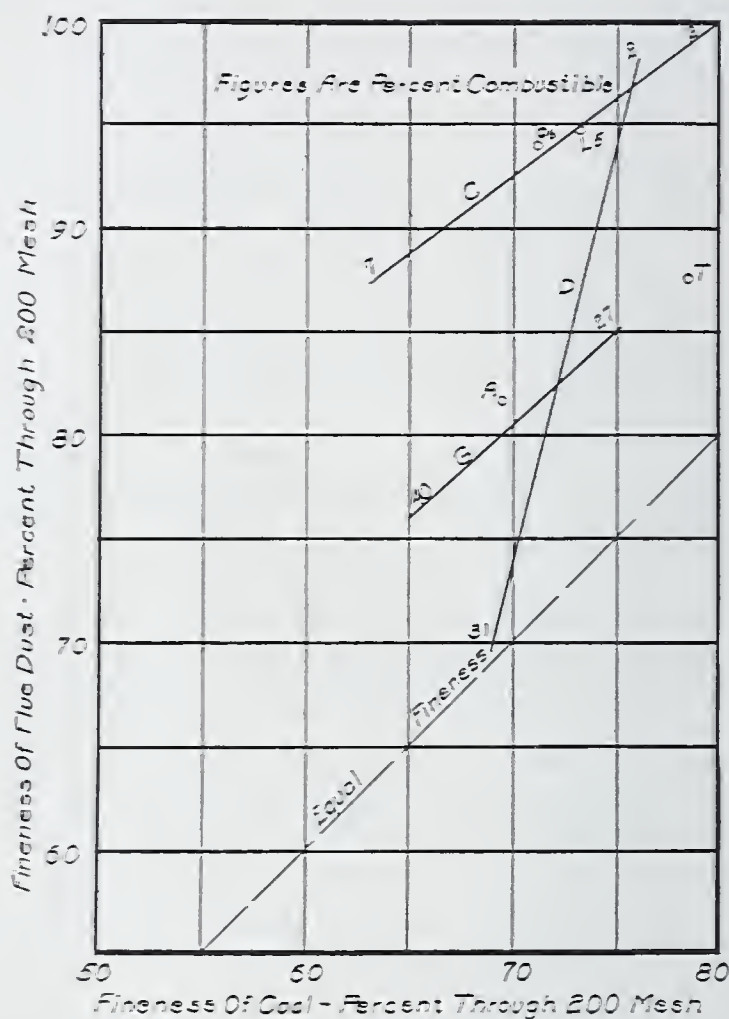


FIG. 11. COMPARISON OF COAL FINENESS WITH FLUE DUST FINENESS

Furnace *T* shown in Figure 22, burns semi-bituminous coal. It has no water cooling and is operated at relatively high furnace temperatures, and yet the carbon loss is higher than other cooler furnaces burning bituminous coal.

Furnace *A* as shown in Figure 16 has a combination of vertical

and horizontal firing, and in which bituminous coal is burned. This is a relatively hot furnace, as the front wall only is water cooled. This front wall was recently changed from air cooled to water cooled construction to enable the rating to be increased from a maximum of 16,000 to 24,000 B.t.u. per cubic foot.

The curves for furnace *A* in Figures 1 and 2 show the carbon loss increasing from 0.3 to 0.8 per cent with an increase in rating of from 14,000 to 24,000 B.t.u. per cubic foot and with the time in the furnace

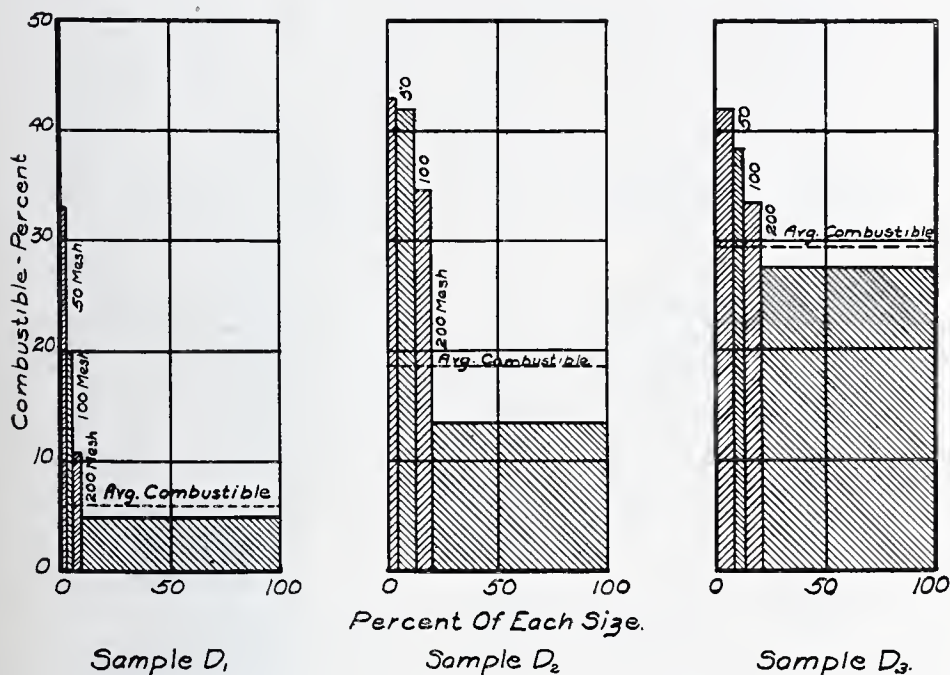


FIG. 12. DISTRIBUTION OF COMBUSTIBLE FOR DIFFERENT FLUE DUST FINENESS

There is evidence of too low excess air, for the portion passing through 200 mesh and having a high combustible would otherwise have been burned.

reduced from 5.1 to 2.7 seconds. The directions of these curves compared to similar curves for furnaces *B* and *C* would indicate that furnace *A* gives lower carbon at lower ratings due to the higher furnace temperature, and higher carbon loss at higher ratings due to less turbulence from the flare type burners at higher ratings.

Furnace *C* as shown in Figure 18 is somewhat similar to furnace *A* except it is completely water cooled on all four sides with hopper bottom. It has turbulent burners and the three curves plotted in Figures 1 and 2 are taken from the detailed data in Figure 3, these

data being taken during extensive and carefully conducted tests wherein three kinds of coal were burned. It is noted that the carbon loss is at a minimum at about 18,000 B.t.u. per cubic foot or a time in furnace of about  $1\frac{3}{4}$  seconds. At higher ratings the carbon loss increases, principally due to the higher velocities and shorter period

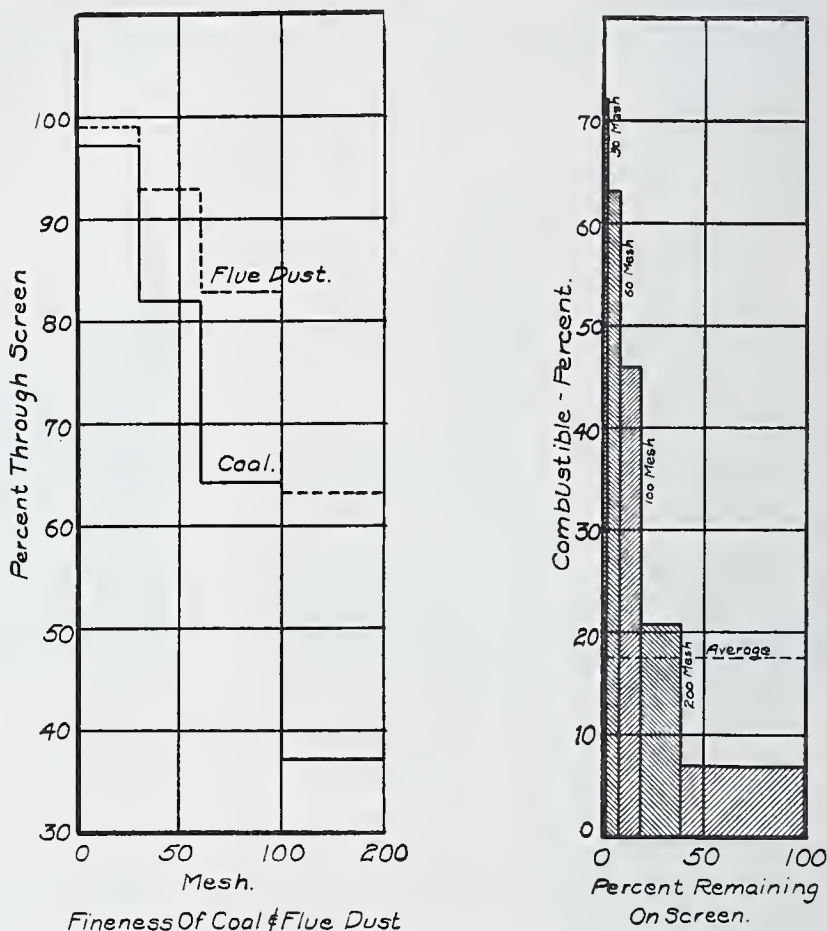


FIG. 13. SCREEN AND COMBUSTIBLE TESTS OF COAL AND FLUE DUST. COAL FROM HIGH SPEED IMPACT MILL AND FLUE DUST FROM SAME COAL

of time for combustion to take place, while at the lower ratings the slight increase in carbon loss is no doubt due to the cooler furnace and the lesser turbulence of the burners when operating at the lower air velocities.

It was noted that the combustible in the flue dust is somewhat lower when burning one coal than when burning the others. This will be explained later in connection with the fineness of the coal.

Furnace *B* represented in Figure 17, shows the lowest heat loss at about 22,000 B.t.u. per cubic foot increasing to something over 1 per cent at the low as well as at the high rating. This being a water cooled furnace no doubt shows the same characteristics in this respect as commented upon in connection with furnace *C*, the total carbon loss being higher however, due to slightly coarser coal, as will be later explained.

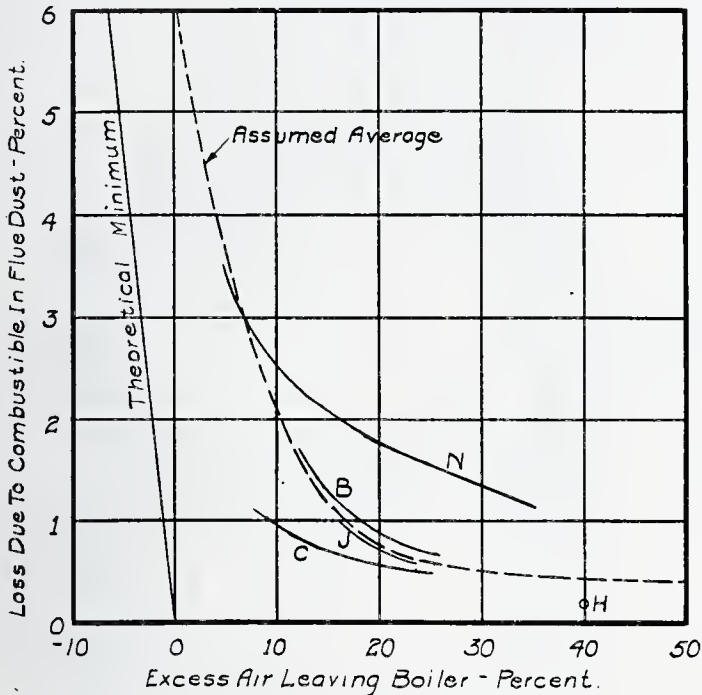


FIG. 14. EFFECT OF EXCESS AIR ON FLUE DUST COMBUSTIBLE LOSS

Furnace *L* plotted only as a point, is very similar to furnace *C* and it is noted the carbon loss at 19,000 B.t.u. per cubic foot is in close agreement with the other results.

Furnace *H*, as shown in Figure 20, is similar to furnace *C* in Figure 18, but is direct fired, using the same coal as *K* with furnace *C*. It is noted the carbon loss is somewhat lower than from furnace *C*. This may be due to the advantages of direct firing over the bin and feeder system. Furnace *H* is also operating with a slightly higher percentage of excess air than furnace *C* as shown in Figure 14.

Furnace *F* as shown in Figure 19, has a volume of only 255 cubic feet, and has an average flame travel of about 9 feet. As noted from

details of Figure 4 both high volatile and low volatile coals have been burned successfully with a carbon loss which is remarkably low considering the high B.t.u. per cubic foot and the very short time in furnace as shown in Figure 2. A carbon loss of 1.6 per cent with 75,000 B.t.u. per cubic foot and less than four-tenths of a second

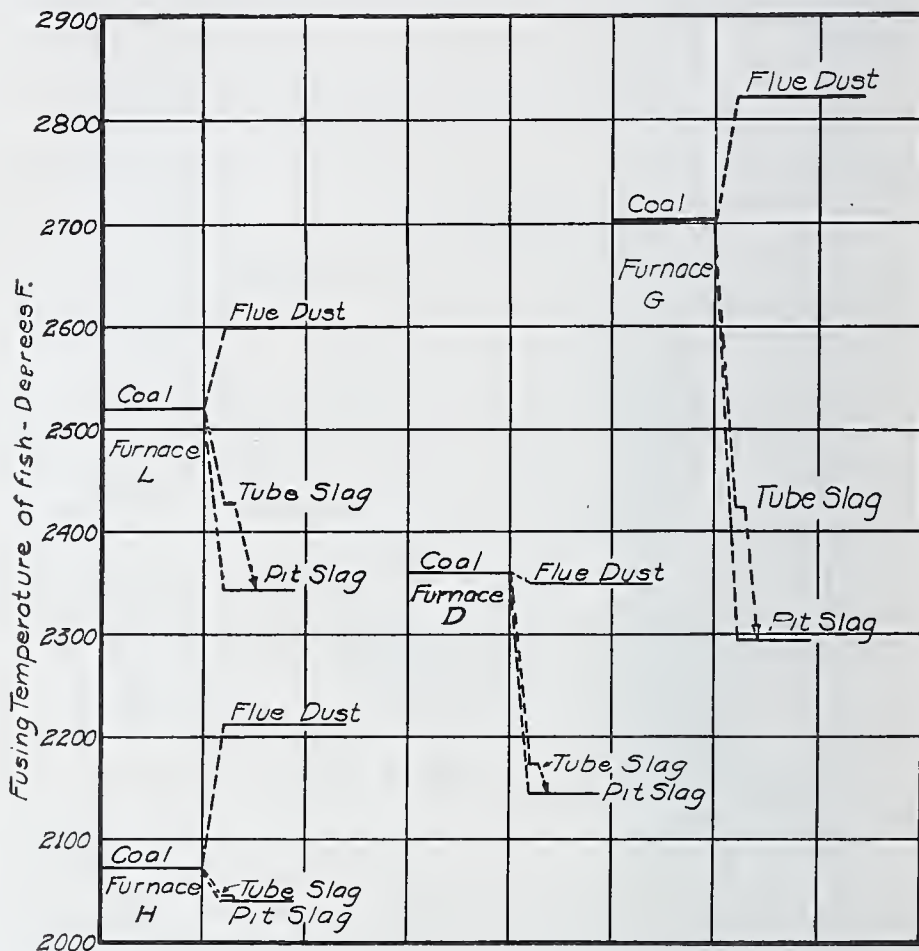


FIG. 15. FUSING TEMPERATURE OF REFUSE COLLECTED AT DIFFERENT POINTS IN SETTING COMPARED TO THE FUSING TEMPERATURE OF THE COAL ASH

average time within the furnace indicates decidedly the advantage of having all the secondary air enter at the burner and of securing effective turbulence in the mixing of it with the primary air and coal. The furnace is also hot, as there is no water cooling except the heat absorbed from the boiler tubes about 3 feet above the center of the burners.

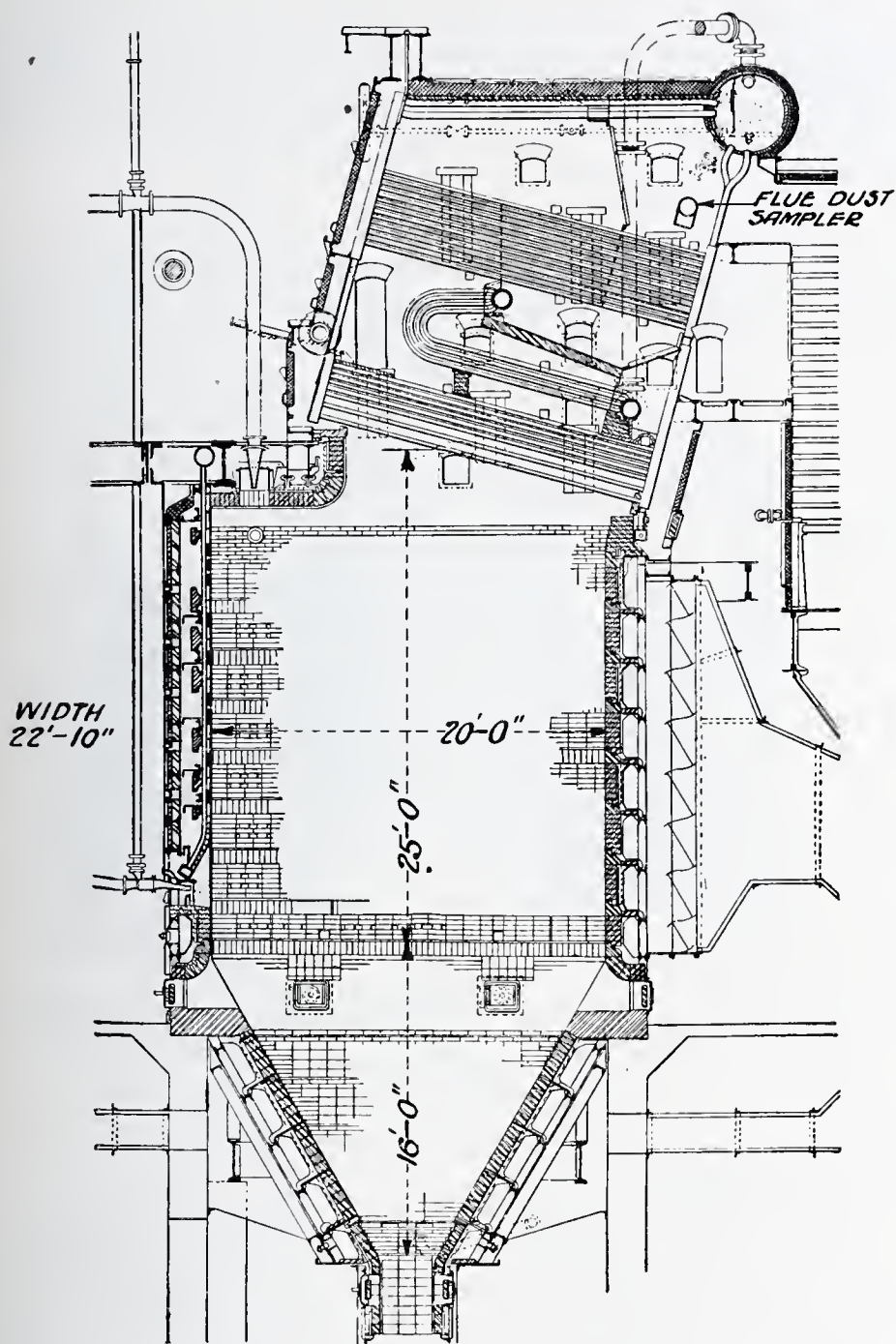


FIG. 16. FURNACE A. REFRACTORY HOPPER AND FURNACE WITH WATER COOLED FRONT WALL

From these curves we can well see that temperature, turbulence and time are important factors in producing most complete combustion within the furnace. However, other factors, such as the character of the coal, fineness of pulverization and excess air are also contributory to this result and they will be discussed later.

#### ASH IN COAL AND COMBUSTIBLE IN FLUE DUST

Before going further it might be well to bring out forcibly the relation between percentage of combustible as determined in the flue

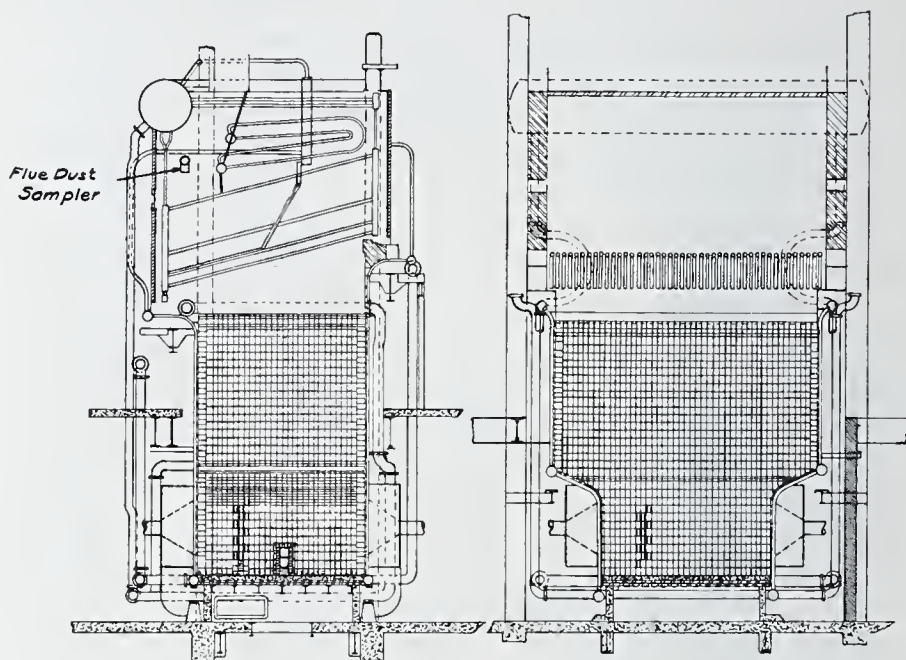


FIG. 17. FURNACE B. SLAG TAP FURNACE CONSTRUCTION WITH TANGENTIAL FIRING. PROTECTED WATER COOLED WALLS. SOLID FLOOR OF SUITABLE MATERIAL SUCH AS DOLOMITE

dust samples and the carbon loss as expressed in per cent of total heat in the coal as fired.

Figure 5 shows a diagram plotted for different percentages of combustible in the flue dust sample, for different percentages of ash in the coal, and for different percentages of ash escaping as flue dust. From this it is noted that the low ash coal can have a rather high percentage of carbon in the flue dust and still not increase the carbon loss excessively. This should be a strong argument against comparing results from different plants on a basis of the percentage of combustible in the flue dust sample alone.

Figure 6 brings out the same point by plotting the relation on a different basis. From this it is obvious that if a fuel which had no ash whatever is burned, then any flue dust samples would always show 100 per cent carbon. The ash in fuel is carried through merely

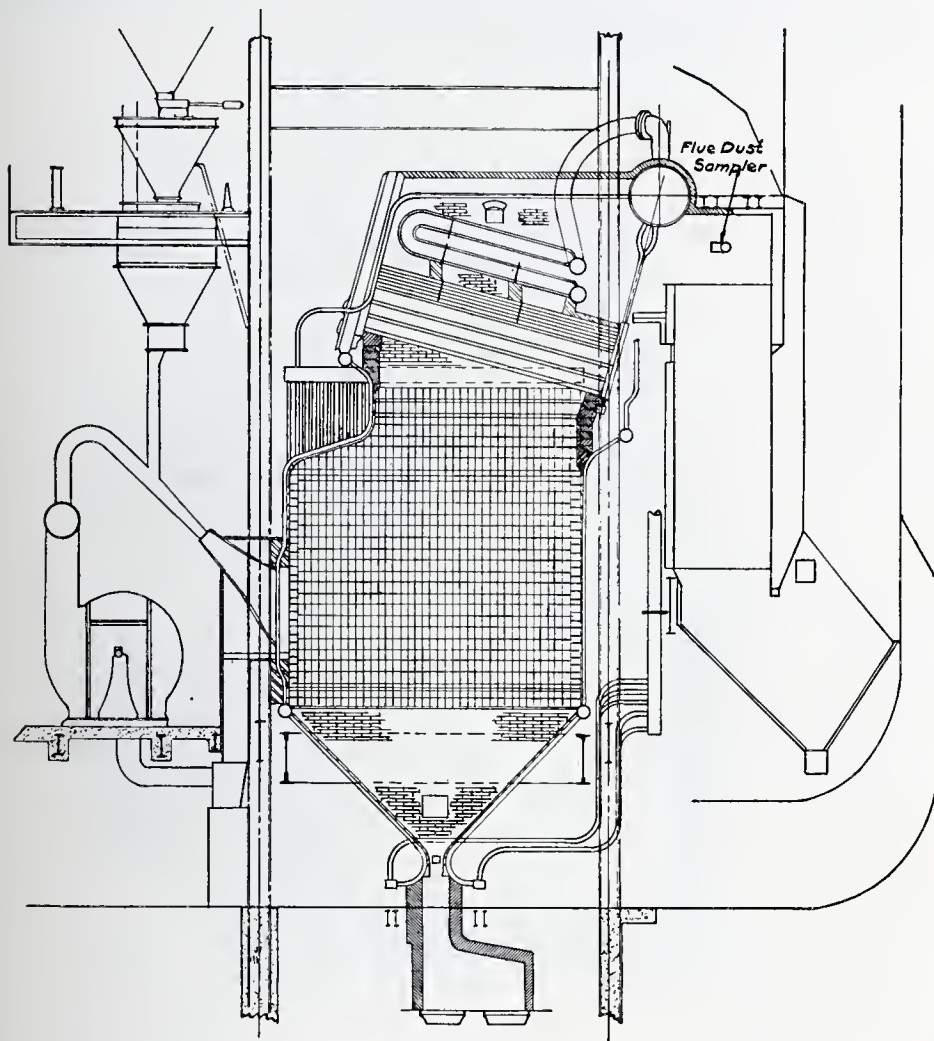


FIG. 18. FURNACE C. WATER COOLED HOPPER AND FURNACE WALL CONSTRUCTION. ASH SLIDES DOWN THE SMOOTH SURFACE INTO THE PIT

as a dilutant, and the carbon loss is no doubt quite independent of the percentage of ash in the fuel, although as shown by plotting data from furnaces *A*, *B* and *C* in Figure 6, there is a change in the percentage of combustible in the flue dust for different percentages of

ash in the coal. These curves follow the same general direction as the iso-loss contours.

There is a possibility that with high ash coals the loading of the gases increases the carrying effect slightly so that a little more carbon loss would take place than with the lower ash coals, although there is no data at hand to bear out this supposition.

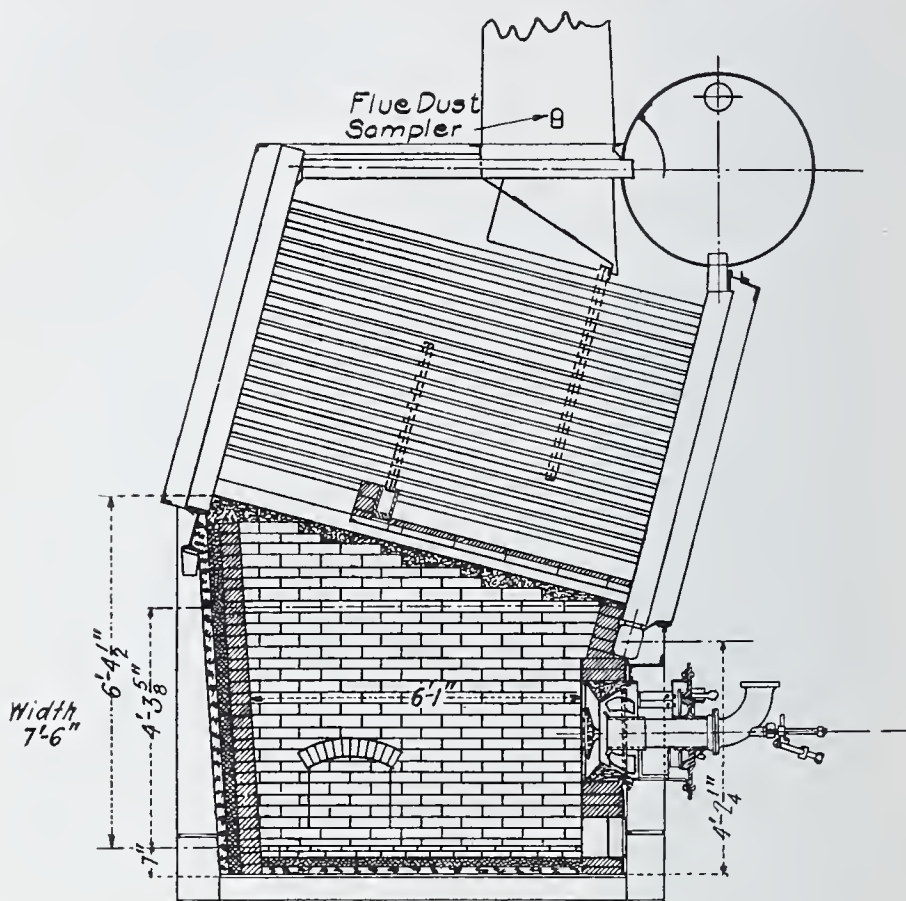


FIG. 19. FURNACE F. PULVERIZED COAL FIRED MARINE BOILER

### FINENESS OF PULVERIZATION

As previously mentioned, the fineness of pulverization of the coal has a noticeable effect upon the carbon loss. Detailed data from furnaces *A*, and *C* are plotted in Figure 7, and furnace *D* in Figure 8. These are given in detail merely to show the individual points in plotting these curves as these three furnaces bring out some interest-

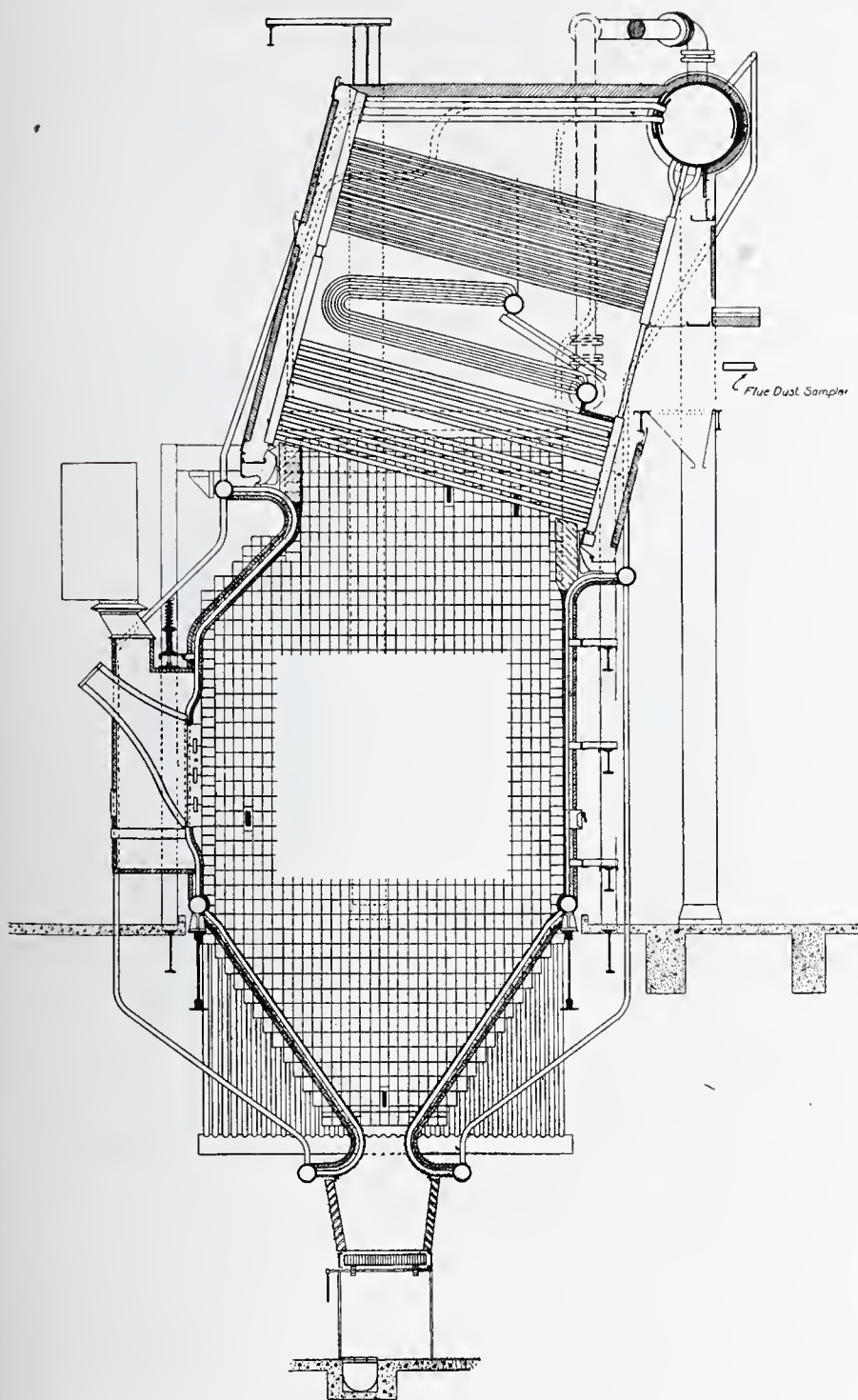


FIG. 20. FURNACE H. DIRECT FIRED WATER COOLED FURNACE AND SMOOTH SURFACE WATER COOLED HOPPER

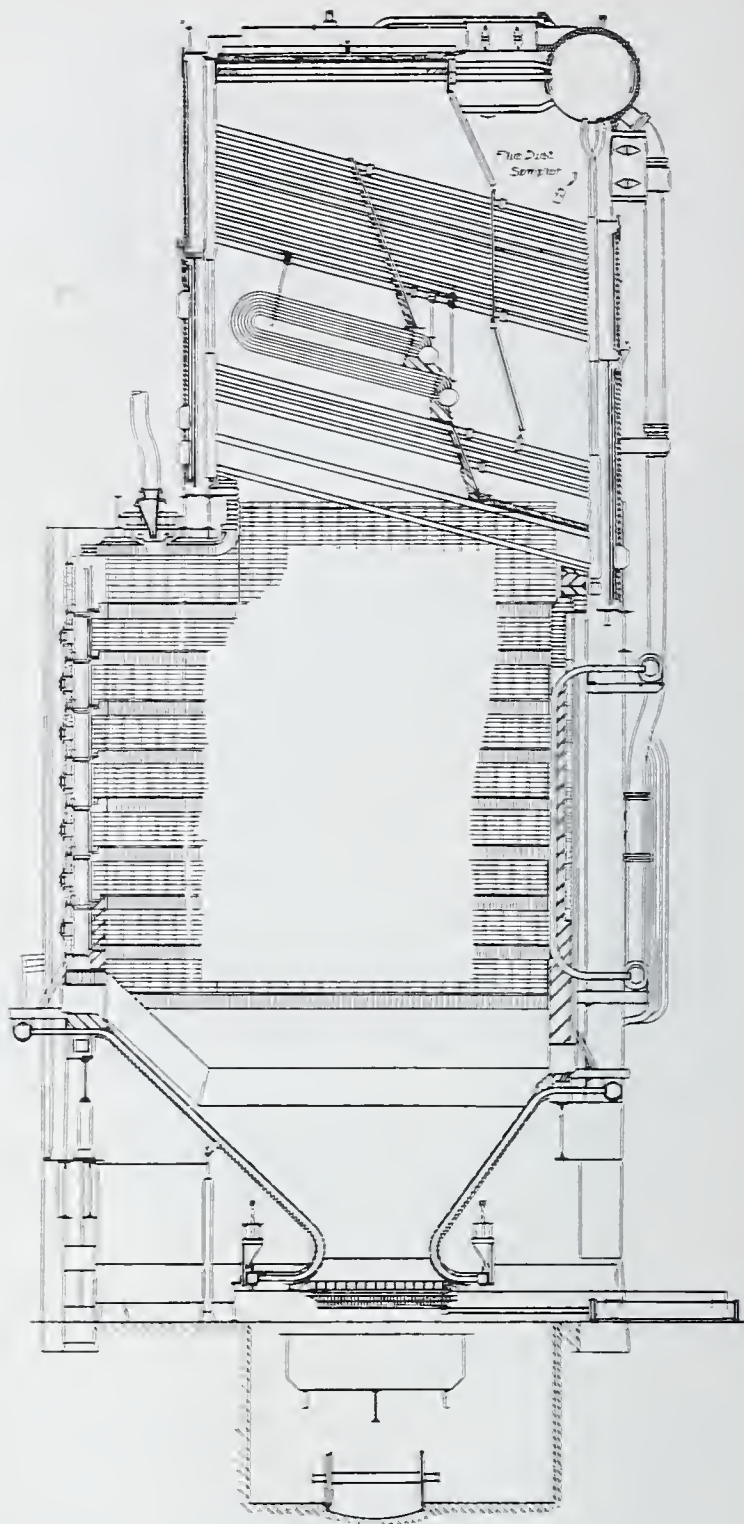


FIG. 21. FURNACE M. SMOOTH SURFACE WATER COOLED HOPPER. AIR COOLED REFRACTORY FURNACE WALLS

ing features when compiled on the composite curves of Figure 9. It is noted that these three curves for furnaces *A*, *C* and *D* coincide with 3 per cent combustible in the flue dust and a coal fineness of 76 per cent through 200 mesh. From this common value there is a

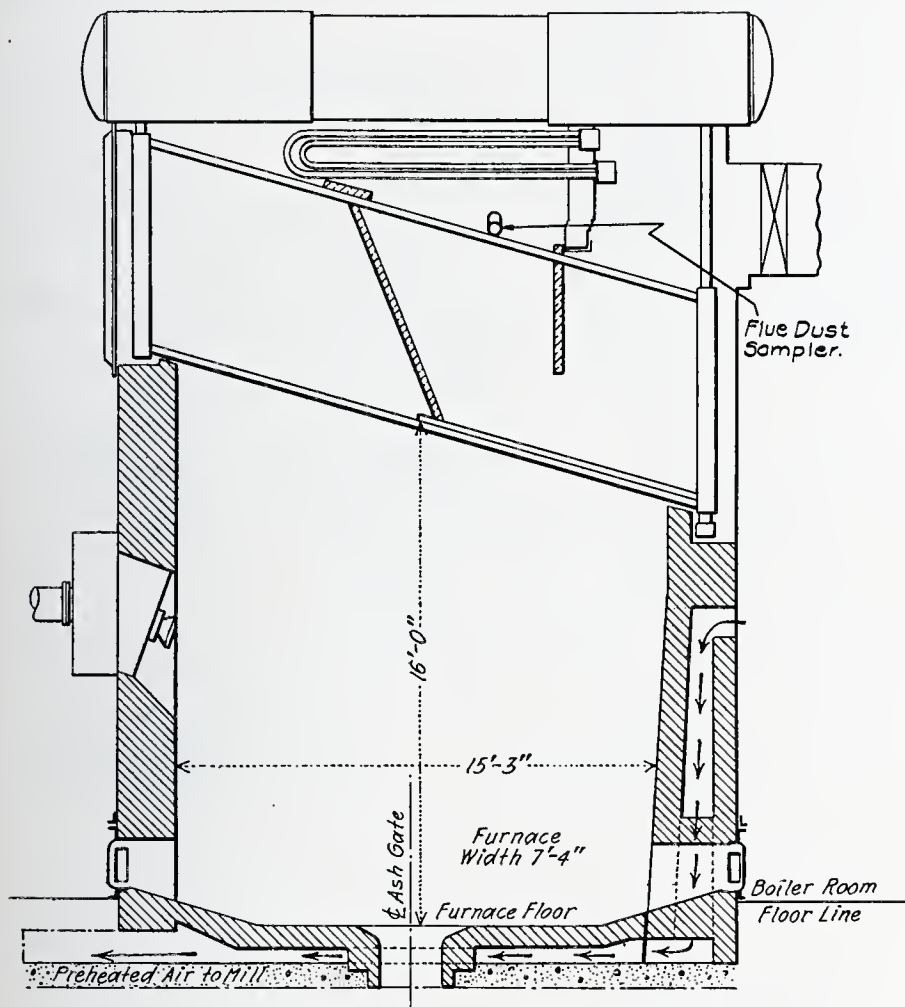


FIG. 22. FURNACE T. FLAT BOTTOMED REFRACTORY PULVERIZED COAL FURNACE

wide divergence in the direction of the lines when plotted between per cent of combustible in flue dust and fineness of coal as expressed in percentage through 200 mesh. Furnace *C* with turbulent burning and water cooled walls, has a comparatively flat curve showing an increase to only 6 per cent combustible at 63 per cent through 200

mesh. This curve includes three coals, *K*, *P* and *Y*, but confined to the tests wherein the rating was between 10,000 and 20,000 B.t.u. per cubic foot. The data for furnace *A* as plotted in the lower part of Figure 7, were taken from tests especially run to determine the

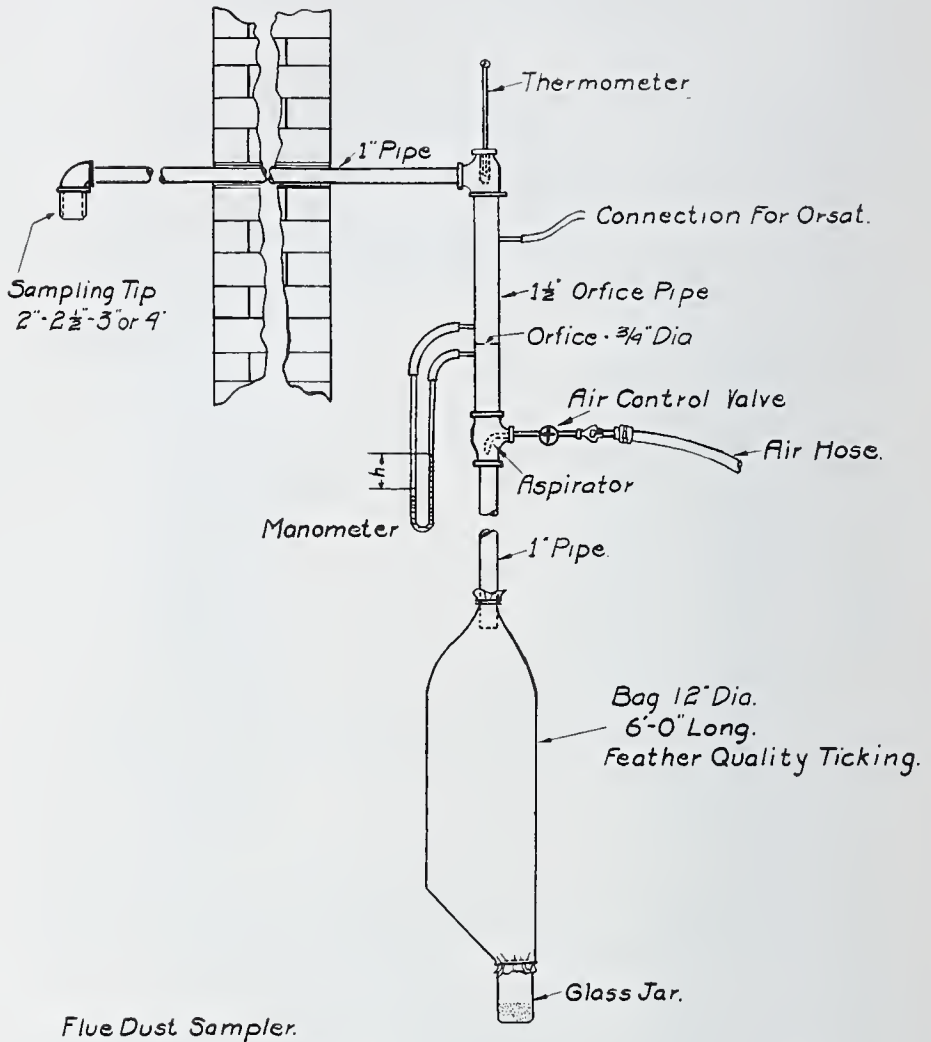


FIG. 23. FLUE DUST SAMPLER AND TYPICAL METHOD OF INSTALLING

effect of fineness. The normal preparation in this plant is between 70 and 75 per cent through 200 mesh, but in order to determine whether or not such a degree of pulverization was required, tests were made with coal as coarse as 60 per cent. The points are some-

what scattered so that there may be some difference of opinion as to just where this line should be drawn. More data on this subject are being obtained in this plant.

Furnace *D* is very similar to furnace *C*, having the same type of burners, approximately the same rate of combustion and similar coals, yet the carbon loss increases very decidedly with slight changes in fineness, and although the average fineness is better than either boilers *A* or *C* the carbon loss is much higher. The reason for this is closely associated with intensive slagging of boiler tubes and low excess air, which will be discussed later after reviewing some of the data in subsequent curves.

Curves from furnaces *E*, *F* and *R* in Figure 9 are substantially parallel to *A* but with a slightly higher combustible, while furnaces *B* and *L* have curves more nearly parallel to furnace *C*. Other furnaces, such as *Q* and *S* have averaged points that are in line with a similar furnace *A*.

A study of the effect of coal fineness upon combustible in the flue dust could be made more easily if it could be definitely known whether a 50 mesh or 200 mesh was a better standard. The results from three furnaces on which most data were obtained, namely *A*, *C* and *D*, are included in the curves in Figures 9 and 10. These curves are in agreement as to the effect of fineness on flue dust combustible, but a study on the basis of the percentage remaining on 50 mesh or the percentage through 200 mesh does not show conclusively in favor of either standard. These data are from coal fineness tests made on pulverized coal samples which showed corresponding changes in fineness at both ends of the fineness scale and which were from similar classes of mills. Further study is necessary to determine whether or not the combustible loss appearing in the flue dust samples originates in the coarse coal or in the 200 mesh size. Flue dust samples obtained under conditions existing where different types of pulverizers are under consideration where the per cent of one size, say that through 200 mesh, is kept constant while the per cent remaining on 50 mesh size is varied and vice versa, will give valuable information. We believe however from some observations and data available that the percentage through 200 mesh and finer should be kept high and that in either case carbon loss is increased materially by the larger sizes or those sizes over 50 mesh.

## FINENESS OF FLUE DUST

Figure 11 is an interesting study of the relative fineness of the flue dust and the coal from which the flue dust is formed. The forty-five degree diagonal line labeled "Equal Fineness" represents the relation if the dust screened the same as the coal. This is not a likely result, as the coal in burning completely would be reduced to a smaller piece of ash which is usually fused into a vitrified bead or globule in a furnace that has a temperature higher than the fusing point of the ash.

The flue dust from furnace *C* shows more than 20 per cent additional weight passing through 200 mesh than the coal being burned. In other words, from the burning of coal having 80 per cent through 200 mesh, the flue dust shows 100 per cent through 200 mesh, and the curve for varying fineness is substantially parallel to the equal fineness standard. The figure at either end of the curves or at a point represent the percentage of combustible in the flue dust sample. It is noted that the results from practically all furnaces having combustible between 2 and 10 per cent carbon lie very closely in the zone of furnace *C* with about 20 per cent additional weight passing through the 200 mesh.

Curve *G* which represents 30 per cent combustible in the flue dust shows only 10 per cent more through 200 mesh than does the coal. The ash from furnace *D* is 22 per cent finer than the coal when it has 2 per cent combustible, while it is substantially equal to the fineness of the coal with 31 per cent combustible. This is a natural consequence of particles of coal swelling to pieces of coke and then holding substantially their original shape or at least having a much larger volume than if they had been completely burned to ash and the condensed fused ash alone carried away as flue dust. It therefore seems that the relationship between the fineness of the coal and the fineness of flue dust collected in the sample should properly check with the percentage of combustible.

## EXCESS AIR

As the curves from furnace *D* plotted in Figures 9, 10 and 11 digress widely from similar data from the other furnaces, and samples of flue dust were still available, further study has been made and some results are shown in Figure 12. Several samples of flue dust were taken from each of three groups with low, medium, and high

combustible content, represented as  $D$ ,  $D2$  and  $D3$  respectively; each sample was screened on 50, 100, and 200 mesh screens and the percentage of each size determined and each size was also analyzed for combustible.

The flue dust  $D1$ , having low combustible, when screened showed large percentages through 200 mesh and very small quantities on 50 or 100 mesh. The combustible was largely confined to the coarser sizes. The flue dust samples with high combustible content,  $D3$ , showed relatively large percentages coarser than 50 and 100 mesh and these were also high in combustible, some exceeding 50 per cent. The most interesting point, however, is that the portion passing through 200 mesh is above 26 per cent combustible, thereby indicating that there was a deficiency of air or at least a minimum of excess air in the furnace or else the fine coke dust would have been more completely burned.

This boiler has an arrangement of tubes and is so baffled that slag readily accumulates thereby choking the gas passage. The increased draft suction above this choked area induces leakage of air through the brickwork, door cracks, etc., so that the operating guide as to excess air is in error in showing the actual excess, or deficiency of air, in the furnace proper. Often the excess air leaving the boiler was less than 15 per cent, any lower excess air in the furnace would retard the combustion of the particles of coke and still further accentuate the slagging of the boiler tubes.

Figure 13 gives results from screen tests of coal from a high speed impact mill, and also gives similar screen tests of the flue dust from this same coal. It is noted that there is an increase in the percentage through each of the screens and that there is 26 per cent more flue dust through 200 mesh than there was coal. This 200 mesh flue dust contained only 7.2 per cent combustible while that on 30 mesh screen contained 72 per cent combustible and the entire weighted sample gave 17.5 per cent combustible. The data for Figure 13 is taken from the Prime Movers Committee report of August, 1928, on Pulverized Fuel.

Figure 14 shows a few data relative to variations of carbon loss with excess air. This is a subject which has not been as thoroughly investigated as it deserves. Many furnaces without water cooling have operated with 30 to 60 per cent excess air in order to hold furnace temperatures down and prevent erosion of walls. In other cases the percentage of excess air has been kept higher for reasons

other than most efficient combustion, such as prevention of tube slagging. It is obvious that when a theoretical amount of air is supplied to the furnace that the efficiency of mixing cannot be 100 per cent, therefore some unburned fuel will escape, and as the theoretical excess air is approached this loss must necessarily increase rapidly. There is no question but that the residue most difficult to burn is the fixed carbon in finely divided form existing in burning pulverized coal as well as in sparks and flue dust from stokers. In Figure 1 the results shown for anthracite coal shows this very plainly and with other coals the greater the percentage of fixed carbon and the denser its structure the more difficult it is to burn in a given furnace.

TABLE III  
SHOWING PERCENTAGES OF TOTAL ASH IN COAL WHICH ARE COLLECTED  
FROM FURNACE

	TOTAL ASH COLLECTED FROM FURNACE
	<i>per cent</i>
Furnace B.....	30
Furnace C.....	40
Furnace F.....	17
Furnace R.....	12
Furnace U.....	20

#### DISTRIBUTION OF ASH

Table III shows distribution of ash in some of the different furnaces listed in this paper. The difficulty of obtaining complete data at different ratings on all various furnaces is recognized by all, hence the meagerness of this information. However, it appears that furnaces *B* and *C*, wherein the rates of combustion are high and the fusing temperature of ash relatively low that it is deposited in a sticky or molten form on the walls and to some extent on boiler tubes from which it runs and drops into the lower part of the furnace.

In furnace *B* it is removed as molten slag as previously described, while in furnace *C* it often runs in a molten condition through the throat of the hopper where it finally chills and a large per cent is collected and retained in this form. It is, of course, desirable to recover as much ash as possible in the furnace, providing suitable means for removal are available.

Figure 15 shows an interesting study in the fusing temperature of ash in the coal in comparison with that collected from different parts of the furnace and the flue dust. For instance, in furnace *L*, a fusing temperature of 2,520°F. for the coal ash has a corresponding flue dust fusing temperature of 2,600°F., while the coarser particles or the slightly lower fusing temperature particles which are sticky when they reach the boiler tubes have a fusing temperature of 2,430°F.; this latter represents results of samples taken from the accumulation on tubes. In all boilers there is a certain amount of such accumulation, most of which can be dislodged by soot blowers or occasional lancing. Fused or solidified ash in the form of slag which is taken from the pit has a fusing temperature of 2,340°F.

Furnace *D* shows coal with a fusing temperature of ash of 2,360°F., while the flue dust passing through the boiler has a fusing temperature of 2,330°F. Ash retained on the tubes shows a fusing temperature of 2,170°F., and the molten slag tapped from this furnace has 2,145°F., as its fusing temperature.

Furnace *H* starting with a coal ash fusing at 2,070°F., gives a relatively high fusing temperature flue dust, namely, 2,210°F., and the slag on the tubes and in the pit fuses about 30 degrees lower than the ash in the coal.

It is obvious that this is a very interesting field for further study and investigation, and one which is very active at the present time with the higher capacities and the attention which is drawn to the slagging of boiler tubes.

Everyone realizes that coal ash is composed of a variety of material of various sorts, and the fusing temperature determination made on the average sample of coal may contain some particles of relatively high fusing temperature and some of rather low, and in some cases the fluxing action of one with another may produce a composite result that is different from what would obtain if these particles were classified according to their composition.

When pulverizing coal and firing it into a furnace there are several things which lead to such classifications.

The coarser coal is usually that which is harder to pulverize and may contain a larger percentage of pyrites and other low fusing or fluxing materials which will tend to drop out and be accumulated in the ash pit or slag bath.

Of the other particles which are small enough to float with the gases, those which have a lower fusing temperature will naturally be

sticky and more likely to adhere to the furnace walls or the boiler tubes than the high fusing temperature particles, which will be dry and dusty and will pass on through.

In connection with the slagging of tubes, the size of the particles also has an important effect, for with two particles of the same fusing temperature the larger one will remain sticky while the smaller particles will radiate enough heat to the boiler tubes as it approaches and thereby be cooled below the sticky point by the time it strikes the tube, and will then rebound and pass on through between the tubes.

### FLUE DUST SAMPLER

The equipment used in taking flue dust samples from the boiler furnace is shown in Figure 23. The sampling tip is so located in the boiler setting as to get a representative stream of gases, preferably flowing upwards, and the opening in the sampling tip is pointed against the oncoming dust-laden gases.

An aspirator operated by compressed air is used to induce the flow, also a suitable fan has been used with equally good results. An orifice and manometer and a thermometer are available for checking the rate of flow of gases so as to maintain the velocity entering the sampling tip substantially the same as the velocity of gases at the point where it is located.

The flue dust is collected in a large bag filter suspended from the discharge end of the aspirator. A glass jar is attached to the lower part of this bag and most of the dust settles in this jar as it is being accumulated. By shaking the bag the residual dust is deposited into the jar, thereby making it easy to remove and retain the sample with no transfer or loss in the handling of it.

This is usually operated with 50 to 150 cubic feet of gas per minute passing through the orifice. This volume is increased somewhat with the aspirating air. However, even then the velocity through the bag is very low. About half a pint of dust is collected in a two-hour period.

Many other kinds of dust sampling equipment have been used, some with cyclones and various means for separating the dust. The bag filter is preferred as it is very effective and this equipment is simple to operate. Its use will be extended to a great many more installations, as the results obtained from studying the dust, the size, composition, and other characteristics are extremely illuminating in solving the problems of burning coal.

In proportioning the quantity of the samples to the total weight of gases from the boiler, estimates have been made as to the total amount of dust. In the majority of cases this gives a reasonable figure, showing from 25 to 100 per cent of the ash in the coal escaping, but it is believed that sufficient accuracy to determine this point is not yet available.

More attention should be given to the collection of flue dust samples from stokers, for it is quite evident that at higher ratings the carbon loss in flue dust will exceed the carbon loss in the ash pit.

#### SUMMARY

1. The removal of ash from mechanical stokers has been greatly improved and the percentage of carbon lost to the ash pit has been materially reduced.

2. The removal of ash from pulverized coal fired furnaces has been greatly facilitated by water cooled hoppers.

3. The latest method of removing ash is in the form of molten slag.

4. Carbon loss in flue dust from both stokers and pulverized coal fired boilers is an important problem which deserves much more study than it has received.

5. Carbon loss in flue dust from pulverized coal fired furnaces increases with

- a. Anthracite or coal with high fixed carbon.
- b. Coarser pulverization.
- c. Cold furnaces.
- d. Delayed mixture with air.
- e. Low excess air.
- f. High rates of combustion.

6. Slagging of boiler tubes is accentuated by the lower fusing temperature of ash, large size of ash particles and by high temperature and velocity of gases entering the boiler tubes.

## CLINKERING OF COAL ASH IN BOILER FURNACES

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When a relatively large amount of coal is to be purchased for steam generating purposes it is customary to prepare a list of those coals which are available at a reasonable freight rate.

A careful study is then made of the proximate analysis, sulphur, heating value and ash fusion temperature of those coals which are available and a few, perhaps not more than three or four, of the most promising are selected for trial.

A test of several days' duration is made on each coal under actual operating conditions to determine which will give the most economical results and to observe the general behavior of the coals in the boiler furnace.

In some plants, the ability to respond promptly to sudden demands for large quantities of steam or to maintain high rates of combustion for a long period of time without undue clinkering may be more important than high thermal efficiency.

These tests yield information which, when combined with the delivered price, makes it possible to select the most suitable fuel.

This method leaves much to be desired. The preliminary examination of the proximate analysis, heating value, sulphur and ash fusion temperature may lead to the elimination of certain coals which, if given a trial in the plant under operating conditions, might prove to be the most desirable.

Many coals have been condemned because of a high sulphur content. In fact, most coal specifications impose a maximum limit on the sulphur content which eliminates many desirable coals. It will be shown later that a high sulphur content is not a priori evidence that the coal is undesirable.

A low ash fusion temperature may eliminate a coal because of the possibility of clinkering, yet it may burn at high rates of combustion without any serious clinkering if properly managed, while coals having high ash fusion temperatures may give considerable trouble from clinker.

Very often the trial shipment of coal is not representative of future shipments under contract. At any mine there is some variation in

the quality of the coal loaded due to variations of the coal in the seam, to mining methods and to preparation on the tippie. It is reasonable to suppose that a trial shipment will receive more attention as to quality than the regular routine shipments.

The plant tests are usually expensive to make and greatly interfere with the regular routine in the plant. It is usually noted that while these tests are in progress the station efficiency will be somewhat lower than the average.

Purchasing agents and plant superintendents have been looking forward to the time when laboratory tests would be devised which would indicate, with a reasonable degree of accuracy, the behavior of a given coal in a boiler furnace of a given type under given operating conditions.

It is very doubtful if such laboratory tests can be developed because there are so many variables entering into the problem that the number of combinations of these variables becomes almost infinite, but it is believed that if the problem is given the scientific study that its importance warrants, laboratory tests will be developed that will yield much more information than is now available.

#### TOTAL SULPHUR AND FUSING TEMPERATURE

The problem of the fusibility of coal ash and its relation to clinkering in boiler furnaces, like all other problems in which exact scientific knowledge is lacking, is surrounded by beliefs which are stated as facts but which do not remain facts when subjected to an impartial and scientific investigation. A certain coal having a high sulphur content may show a low ash fusion temperature and the conclusion is immediately drawn that all coals high in sulphur have a low ash fusion temperature. This is particularly so when the sulphur is largely of the inorganic form because it can be shown chemically that this form of sulphur will yield compounds which should lower the fusion temperature, yet when the conclusion drawn from this isolated case, or even several cases of a similar nature, is applied in a more general manner it is found to be without foundation.

In Figure 1 there has been plotted from data furnished by the United States Bureau of Mines, the total sulphur-ash fusion temperature<sup>1</sup> relation for over 2000 coals from all parts of the United States, and ranging from anthracite to lignite. While this chart

<sup>1</sup> Throughout this paper, ash fusion temperature means the softening temperature as determined by the standard gas furnace method.

shows most of the high sulphur coals lying in the low fusion temperature region, it also shows many of the low sulphur coals in the same region.

There are 35 points between 2000° and 2100°F. for the sulphur range of 0.5 to 1.0 per cent while there are only 32 points between these two temperatures for the sulphur range of 3.5 to 4.0 per cent.

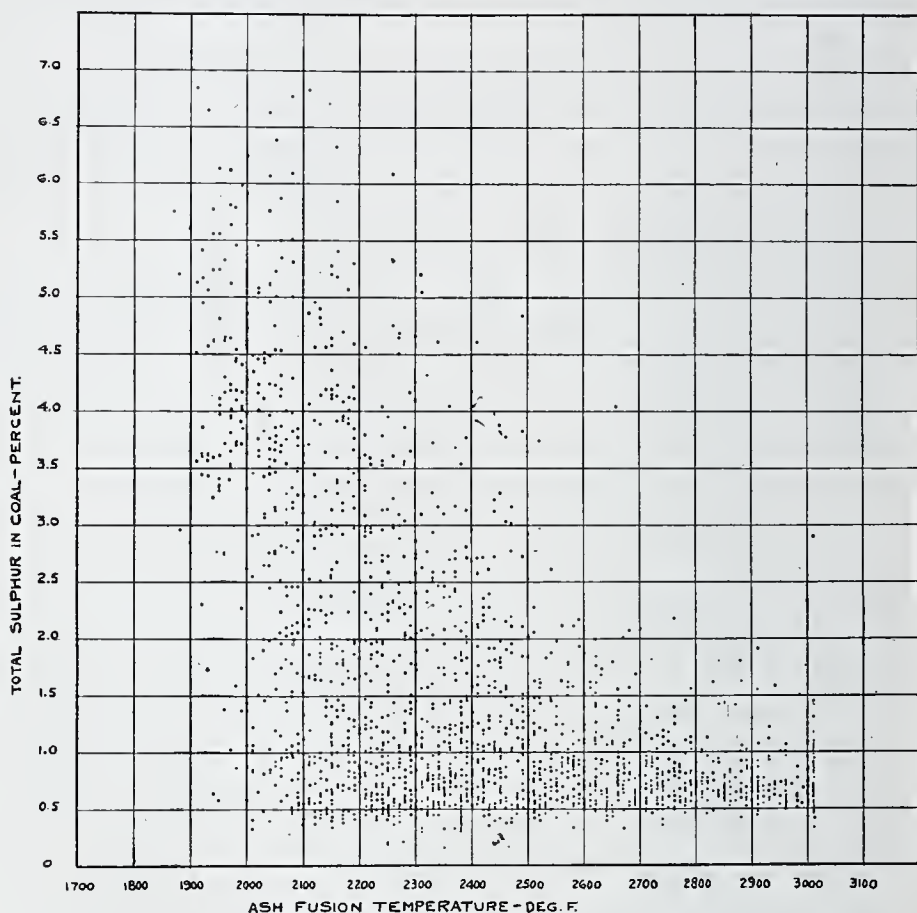


FIG. 1. ALL CLASSES OF COAL

There are 60 points between 2100° and 2200°F. for the sulphur range of 0.5 to 1.0 per cent while there are only 18 points between these two temperatures for the sulphur range 3.5 to 4.0 per cent.

This chart shows conclusively that it is impossible to predict the ash fusion temperature from the sulphur content of the coal. It also shows that the sulphur content of a large percentage of the coals being produced today lies between 0.5 and 1.0 per cent.

Figure 1 included coals from all six of the classifications and since these classes differ greatly from each other, Figure 2 was made for the semi-bituminous group to determine if any better relation between the total sulphur and ash fusion temperature existed for any particular classification.

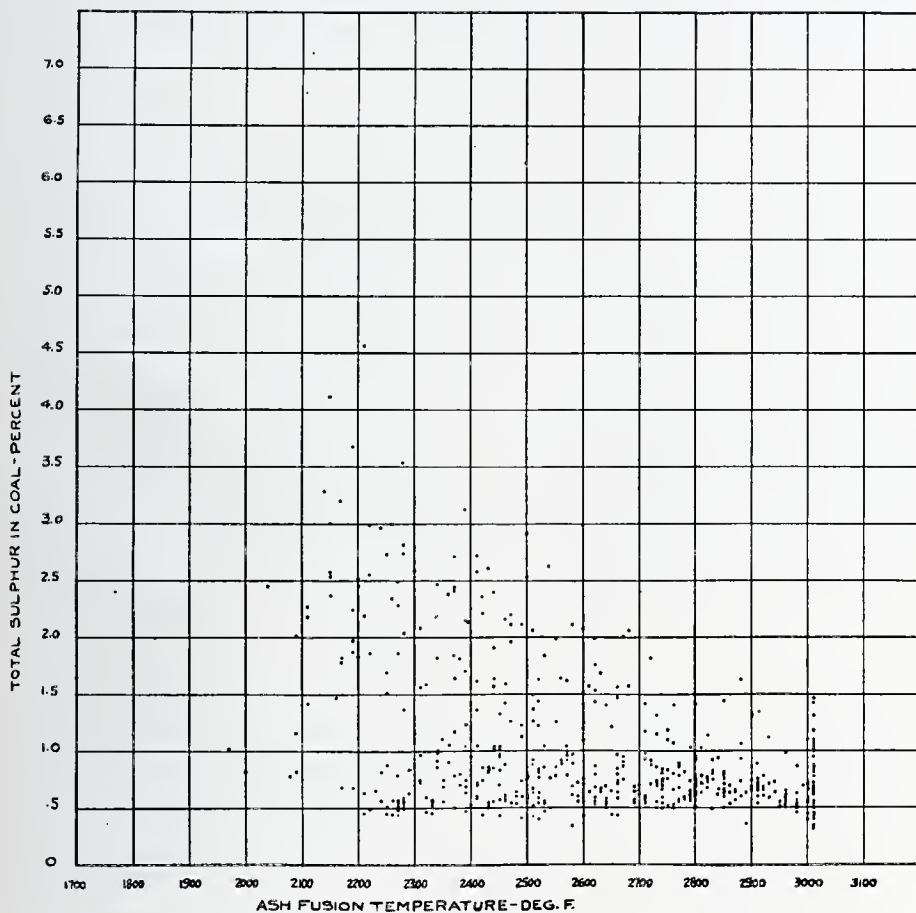


FIG. 2. SEMI-BITUMINOUS

This plot does not yield any additional information and presents about the same appearance as the plot for all coals.

The conclusion could be drawn from these two plots that a high sulphur coal is likely to have a low fusion temperature but the converse is not true that a low sulphur content would indicate a high fusion temperature.

## PYRITIC SULPHUR

It is unfortunate that the bulletin (1) used for plotting the two charts does not give the sulphur forms so that the effect of pyritic sulphur on the ash fusion temperature could be more accurately judged. It is probable that more coals are condemned without trial on the content of pyritic sulphur than for any other cause.

The reason for this is no doubt largely due to the chemistry of iron pyrite when subjected to heat.

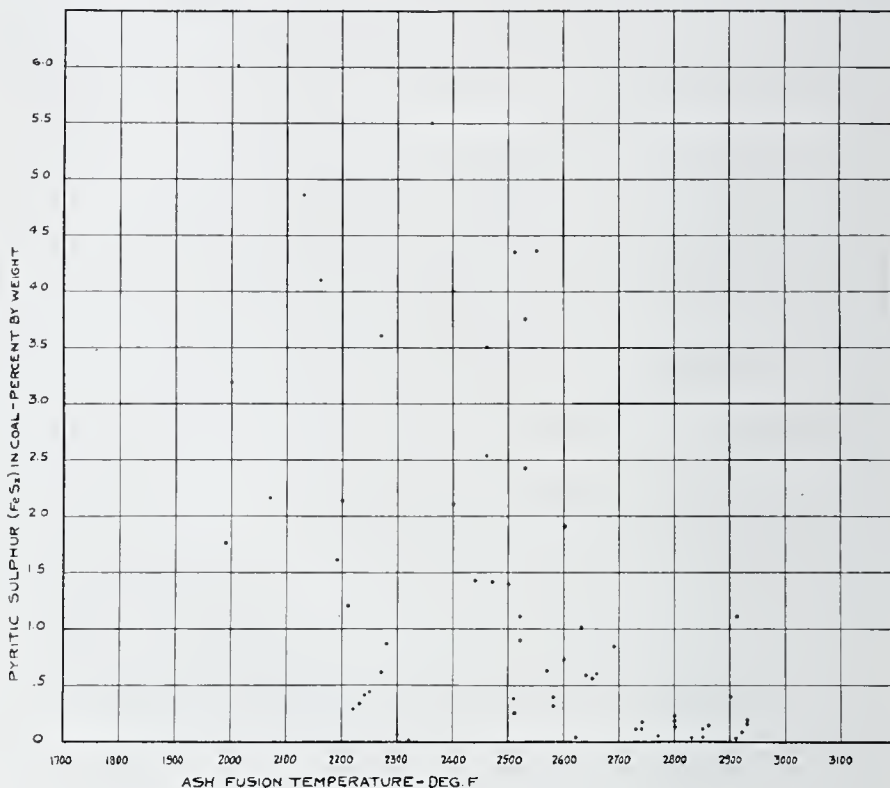


FIG. 3

Dr. Parr of the University of Illinois, who has had much experience with Illinois coal which is usually high in pyritic sulphur, believes that this compound first breaks up into ferrous sulphide ( $\text{FeS}$ ) and free sulphur. The ferrous sulphide fuses at a temperature of  $2190^{\circ}\text{F}$ . and flows freely through the fuel bed and serves as a binder for the slate and other impurities and thus produces clinker. The breaking up of iron pyrite into ferrous sulphide and free sulphur has been observed in burning gob piles but there is no conclusive proof that it does take place in a boiler furnace.

If the pyritic sulphur is heated in an oxidizing atmosphere it will form ferric oxide ( $\text{Fe}_2\text{O}_3$ ) and sulphur di-oxide ( $\text{SO}_2$ ). The ferric oxide unites with the silica forming a high fusion temperature compound. If the atmosphere is strongly oxidizing the iron in the pyrite will appear as metallic iron which will also raise the fusion temperature. If the atmosphere is only slightly oxidizing, the pyrite produces ferrous oxide ( $\text{FeO}$ ) which will unite with the silica to form a low fusion temperature compound. The calcite ( $\text{CaCO}_3$ ) also probably plays an important part in the final effect produced by pyritic sulphur.

It would seem then that conditions which obtain in the boiler furnace are much more important than the amount of pyritic sulphur in determining the amount of trouble to be anticipated from clinker.

Figure 3 shows the relation between the percentage of pyritic sulphur in the coal and the ash fusion temperature for a few coals. Judging from this figure, it would be very unfair to condemn a coal upon its content of iron pyrite. All of these fusion temperatures were obtained in an atmosphere to produce ferrous oxide, so that for comparative purposes, the furnace atmosphere as one factor in the fusion temperature has been eliminated. The plot does show, however, that the fusion temperature will depend upon the relative proportions of all of the compounds in the ash rather than upon any one of them.

#### EFFECT OF OTHER COMPOUNDS IN THE ASH

J. W. Greig (2) has shown that for mixtures of silica with lime or magnesia only a small percentage of alumina was necessary to produce a marked lowering of the fusion temperature and since all four of the above compounds are found in coal ash it is reasonable to assume that they have an important bearing on the fusion temperature as well as the pyritic sulphur.

In a paper by Fieldner, Selvig and Nicholls (3) there are very complete ash analyses of 21 coals. If the melting point curve for the binary system  $\text{Al}_2\text{O}_3$ — $\text{SiO}_2$  as given by Bowen and Greig (4) is drawn and then the actual melting points of the ash plotted on this diagram, using the relative weights of  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  as given in the ash analyses referred to, it is found that all of the points fall very much below the system curve. This would indicate that the oxides of iron, calcium, magnesium, sodium and potassium play an important part in the fusion temperature.

The melting points of the ash were also plotted on the melting diagram for the system  $\text{SiO}_2$  and  $\text{FeO}$  with the same result as for the system  $\text{Al}_2\text{O}_3$ — $\text{SiO}_2$ , that is, the ash melting temperature was very much lower than that of the binary system. This would indicate that the ferrous oxide is not entirely to blame for the lower fusion temperature, but that the other oxides have their influence.

#### RELATION BETWEEN TOTAL ASH AND FUSION TEMPERATURE

There does seem to be a rather definite relation existing between the per cent of alumina in the ash and the fusion temperature as

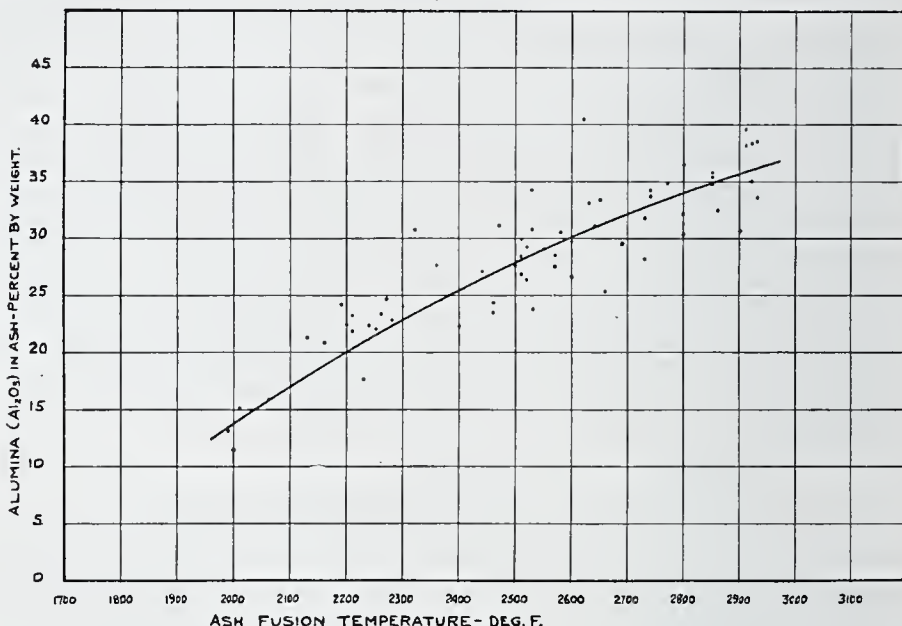


FIG. 4

shown by Figure 4 but there are several points far enough away from the smooth curve to cause one to hesitate to use the alumina as an index of the fusion temperature. Fieldner, Selvig and Nicholls (3) have shown that there is also a general relation between ferric oxide and fusion temperature and the ratio of  $3\text{Al}_2\text{O}_3 + \text{SiO}_2$  to the bases  $\text{Fe}_2\text{O}_3 + \text{CaO} + \text{MgO} + \text{Na}_2\text{O} + \text{K}_2\text{O}$  to fusion temperature but again there are enough scattered points in each case to prohibit the use of these relations for specific cases.

The inherent ash in all coals is from 2 to 4 per cent. All ash in excess of these quantities is the extraneous ash and is composed of

slate, clay, pyrite, etc. Since this extraneous ash is made up of materials which have a relatively high fusion temperature, some have been led to believe that coals with a high ash content will have a high fusion temperature. Figure 5 has been plotted to show that no

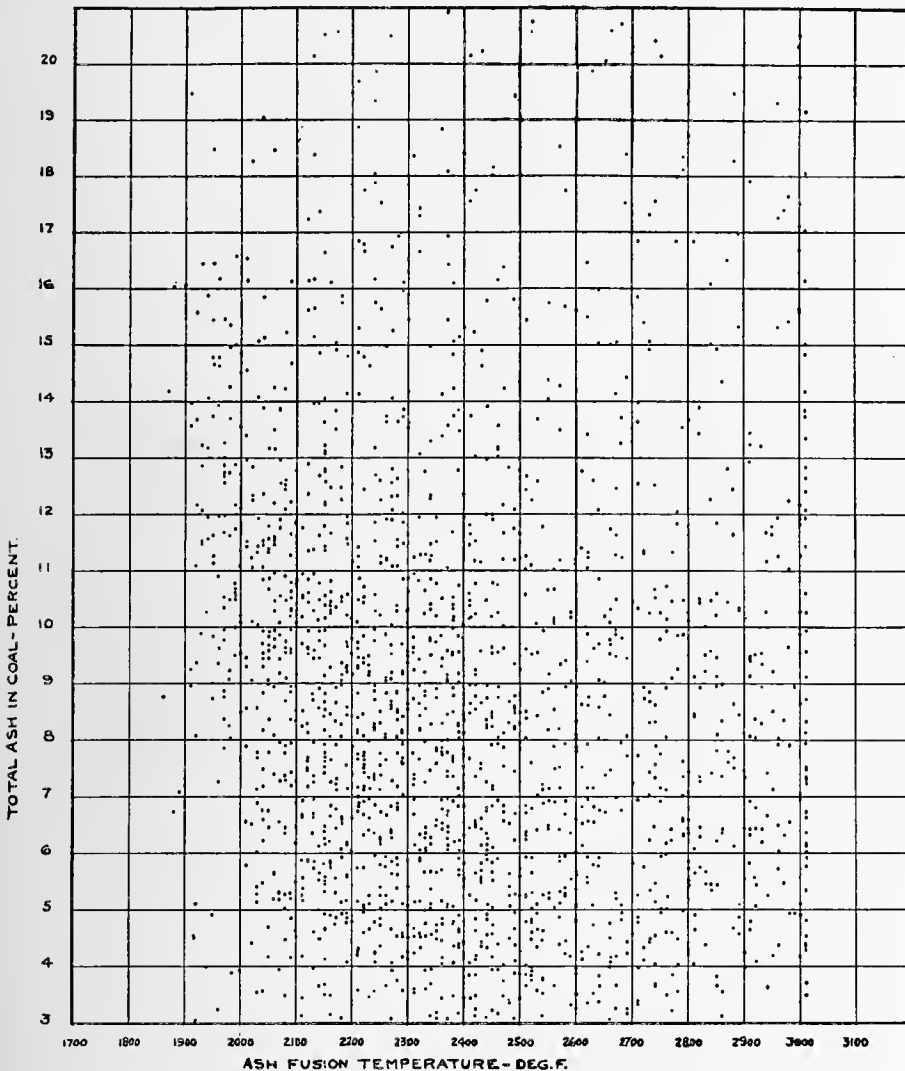


FIG. 5. ALL CLASSES OF COAL

such relation exists and that the fusion temperature cannot be predicted from the ash content. Figure 6 has been plotted for semi-bituminous coal only and shows that such a relation does not exist even for a single class of coal.

MIXED COALS

It is believed by many that when coals are mixed, the ash fusion temperature of the mixture is less than that of any one coal in the mixture.

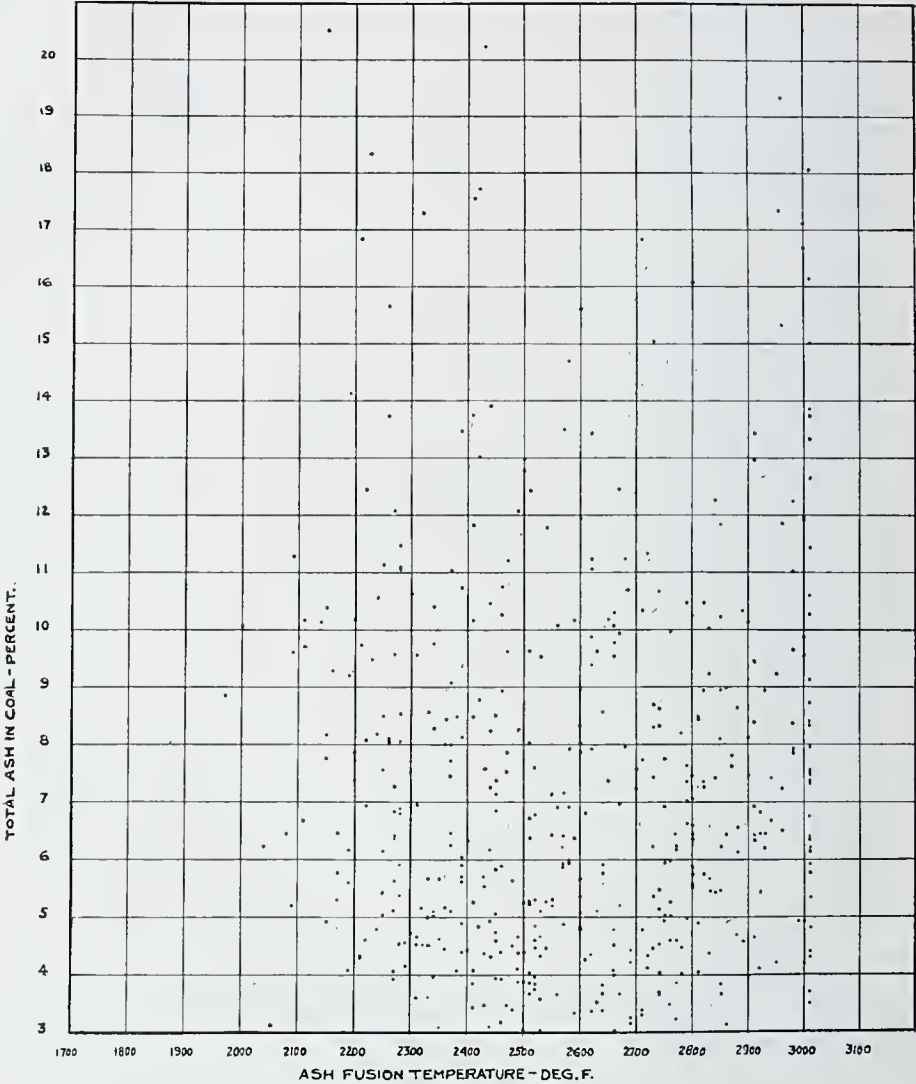


FIG. 6. SEMI-BITUMINOUS

This matter was investigated in a very limited manner and the results are given in Table I. Equal parts by weight were used in all cases. The relative proportions of ash in the coals were used in calculating the average fusion temperature of the mixture. There

is a very close agreement between the observed and calculated temperatures for five of the mixtures. The maximum difference occurs in mixture G and L which gives an observed temperature 150°F. lower than the calculated value. This would indicate some eutectic action between the ashes of these two coals. Mixture B and S shows a difference of 110°F.

TABLE I

COAL	PER CENT ASH IN ORIGINAL COAL	PER CENT PYRITIC SUL- PHUR IN COAL	ASH FUSION TEMPERA- TURE OF ORIGINAL COAL	OBSERVED FUSION TEMPERATURE OF ASH RESULTING FROM MIXTURE OF EQUAL PARTS BY WEIGHT OF ORIGI- NAL COALS	CALCULATED FUSION TEMPERA- TURE OF ASH RE- SULTING FROM MIXTURE, BASED ON RELATIVE WEIGHTS OF ASH IN ORIGINAL COALS
F	12.8	1.61	2,310		
H	11.2	0.73	2,640	2,400	2,460
A	7.1	0.19	2,850		
L	7.2	0.22	2,790	2,800	2,815
P	9.6	0.61	2,440		
Q	6.7	0.11	2,700	2,550	2,545
N	11.3	0.87	2,370		
S	18.5	1.76	2,030	2,070	2,160
K	9.1	1.20	2,390		
N	11.3	0.87	2,370	2,360	2,375
B	7.9	0.18	2,850		
S	18.5	1.76	2,030	2,170	2,280
G	13.9	2.17	2,100		
L	7.2	0.22	2,790	2,190	2,340
C	8.5	1.12	2,520		
D	10.0	1.43	2,490		
E	5.4	0.56	2,670	2,490	2,545

In the three cases where there is considerable difference in the observed and calculated temperatures, the one coal was high in pyritic sulphur and the other low. The eutectic action is probably due to the ferrous oxide as these tests were made in an atmosphere designed to produce this oxide.

Much more work needs to be done along this line, using other proportions in the mixture and other coal combinations. The limited work done would indicate that when coals are mixed the fusion temperature of the mixture will be approximately the average fusion temperature of the two coals. There is not sufficient evidence to justify the conclusion that pyrite in one of the coals will cause a lowering of the fusion temperature.

#### EFFECT OF DISTILLATION ON ASH FUSION TEMPERATURE

During the First International Conference on Bituminous Coal, one of the discussions of a paper on low temperature distillation related an experience of using a coal in a low temperature process which would not produce clinker in a boiler furnace under any conditions but that the coke resulting from the distillation clinkered so badly that it was impossible to use it for domestic purposes. It would have been interesting to have had complete information on this coal but such data were lacking.

It is possible for such an experience as mentioned to occur, but the clinkering was not brought about by the distillation but by the difference in the fuel bed conditions of the coal and the coke. It is not likely that the coal substance itself would furnish any compound which would change the ash fusion temperature. When low temperature distillation becomes more common, it may be necessary to investigate this matter.

There is no way known at present to separate the ash from the coal chemically. Any solvents used to dissolve the coal will also act upon some of the ash and as long as it is necessary to rely upon combustion to separate the ash there will be no way of determining if the coal substance does effect the ash fusion temperature.

In collecting material for this paper a few observations were made in the following manner. Several coals were separately reduced to ash and the fusion temperature of the ash determined. Combinations of equal parts by weight of the ashes from two coals were then made up and the fusion temperature of the mixed ash determined. The same two coals entering into the ash combination were also mixed in equal parts by weight, reduced to ash and the fusion temperature of the ash thus produced determined and checked against the fusion temperature of the mixed ash. Table II shows the results of these observations.

Due to the limited number of observations made it is not safe to draw definite conclusions. It would have been much better to have made the ash mixtures in the same proportions as the ash in the original coals instead of equal parts. The results indicate that it

TABLE II

COAL	PER CENT ASH IN ORIGINAL COAL	PER CENT PYRITIC SUL- PHUR IN COAL	ASH FUSION TEMPERA- TURE OF ORIGINAL COAL	OBSERVED FUSION TEMPERATURE OF ASH RESULTING FROM MIXTURE OF EQUAL PARTS BY WEIGHT OF ORIGI- NAL COALS	OBSERVED FUSION TEMPERA- TURE OF MIXTURE OF EQUAL PARTS BY WEIGHT OF ASH FROM ORIGINAL COALS
F	12.8	1.61	2,310		
H	11.2	0.73	2,640	2,370	2,475
A	7.1	0.19	2,930		
L	7.2	0.22	2,800	2,800	2,865
P	9.6	0.61	2,270		
Q	6.7	0.11	2,730	2,500	2,500
N	11.3	0.87	2,280		
S	18.5	1.76	1,990	2,170	2,135
K	9.1	1.20	2,210		
N	11.3	0.87	2,280	2,310	2,245
S	18.5	1.76	2,030		
B	7.9	0.18	2,850	2,280	2,440
G	13.9	2.17	2,100		
L	7.2	0.22	2,790	2,220	2,445
C	8.5	1.12	2,520		
D	10.0	1.43	2,490		
E	5.4	0.56	2,670	2,530	2,560

*Note:* The values for the fusion temperature of the ash in the original coals in this table are different than those given in Table I because the determinations were made on different samples taken at different times.

makes no difference in the fusion temperature whether the coals are mixed and then reduced to ash or the ashes mixed after combustion. In other words, the coal substances do not react upon each other to change the fusion temperature of the resulting ash.

## EFFECT OF WEATHERING ON FUSION TEMPERATURE

If coal is weathered in the open some of the impurities become soluble and are washed away. The iron in the pyrite may be reduced to oxide and be carried away by solution.

It would be interesting to note what effect this would have on the ash fusion temperature. Information on outside weathered coal was not available but the ash fusion temperature of several coals at the Bureau of Mines had been carefully determined about two years ago. Since that time these coals had been in covered storage, subject to the action of the atmosphere but not to rain or snow. These coals

TABLE III

COAL	ORIGINAL ASH FUSION TEMPERATURE	ASH FUSION TEMPERATURE 2 YEARS LATER	EFFECT OF WEATHERING ON ASH FUSION TEMPERATURE
A	2,930	2,850	Lowered
B	2,930	2,850	Lowered
C	2,520	2,520	No change
D	2,440	2,490	Raised
E	2,650	2,670	Raised
F	2,190	2,310	Raised
G	2,070	2,100	Raised
H	2,600	2,640	Raised
K	2,210	2,390	Raised
L	2,800	2,790	Lowered
N	2,280	2,370	Raised
P	2,270	2,440	Raised
Q	2,730	2,700	Lowered
S	1,990	2,030	Raised

were resampled and the ash fusion temperature determined again. The results are shown in Table III. Out of the 14 coals thus sampled, 9 showed a higher fusion temperature than two years ago and one just 10 degrees lower. There are errors due to resampling and errors in high temperature measurement but when 65 per cent of the coals show a higher fusion temperature after dry storage, it is reasonable to assume that weathering will raise the fusion temperature.

## ASH FUSION TEMPERATURE AND CLINKERING

There are so many factors entering into the subject of clinkering of coal ash in boiler furnaces that it is very difficult to arrive at

anything but very general conclusions from the very limited amount of data available. The type of furnace and stoker, the rate of combustion, the fuel bed temperature, the size of the coal, the distribution of the air supply, the furnace volume, the relative amounts of water cooled and refractory wall surface, the load conditions to be met and the skill of the boiler room labor are all factors in the problem of clinker formation entirely independent of the characteristics of the coal itself.

A coöperative research between the United States Bureau of Mines, the Carnegie Institute of Technology and two large power companies was carried on for two years on the subject of the fusibility of coal ash and its relation to clinkering and the results of this investigation are set forth in two papers (5) (3). This represents about all the information available on this subject. Probably the weakest point in this investigation is that the clinkering tests were made in an experimental furnace that had practically nothing in common with a boiler furnace and the results obtained are purely relative. In defense of this experimental furnace, it may be said that in an investigation of this kind certain conditions must be kept under complete control while others are varied and this cannot be done very well in large scale tests without a great deal of trouble and expense.

In the preparation of this paper some further study was made of the data reported in the papers just referred to with the following results:

There is no relation between the silica in the ash and the ash fusion temperature.

There is no relation between the percentage of coal sinking in a solution of 1.35 specific gravity and the fusion temperature of the ash.

There is no relation between the percentage of coal floating on a solution of 1.35 specific gravity and the fusion temperature of the ash.

There is no relation between the amount of lime ( $\text{CaO}$ ) in the ash and the ash fusion temperature.

(Note: In the following, the word clinker refers to that portion of the refuse passing over 2-inch screen and float and sink portions those parts floating and sinking in a solution of 1.35 specific gravity.)

There is no relation between the clinker expressed as a per cent by weight of the original coal and the ash fusion temperature of the float portion.

When the clinker as per cent by weight of the original fuel is

plotted against the ash fusion temperature of the sink portion smoother curves result than those shown in original papers.

When the clinker as per cent by weight of the original fuel is plotted against the ash fusion temperature of the original fuel smoother curves result than those shown in original paper. There is no relation between the clinker as a per cent by weight of the ash in the sink portion to the fusion temperature of the ash in the sink portion.

There is no relation between the clinker as a per cent by weight of the ash in the sink to the per cent by weight of the ferric oxide in the sink ash.

There is no relation between the clinker as a per cent by weight of the original coal to the per cent by weight of the pyritic sulphur in original coal.

The purpose of this joint investigation was to develop laboratory tests which would make it possible to predict the behavior of a given coal when used as a steam fuel. This result was not accomplished but the work is not a loss because it did show that some of the well known beliefs regarding clinker formation have no scientific foundation. The work also showed that there are so many factors entering into clinker formation that no coal should be condemned on account of any particular characteristic without having been given a trial in the plant under operating conditions.

It is very significant that of the nearly 2000 coals plotted on Figures 1 and 5 about one-half fall between 2000° and 2400°F. fusion temperature, and this range is supposed to be the one in which clinkering will occur. This means that combustion engineers have found methods of satisfactorily handling these coals without producing troublesome clinker. Valuable as laboratory tests may be in selecting coal, there is no information at present which can completely supplant actual plant tests.

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- (3) FIELDNER, SELVIG AND NICHOLLS: The Clinkering of Coal Ash as Related to Laboratory Fusibility Determinations. Transactions of the American Society of Mechanical Engineers, Fuels and Steam Power Section, Vol. 50—No. 8.
- (4) BOWEN AND GREIG: Journal American Ceramic Society, 1924. Equilibrium Diagram for the System Alumina-Silica.

- (5) SELVIG AND NICHOLLS: Bulletin 29, Mining and Metallurgical Department of the Carnegie Institute of Technology. Fusibility of Coal Ash as Related to Clinker Formation.

### DISCUSSION

J. D. ANDREW (Armour and Company Chicago): Can Mr. Bailey give us a little more definite information on the type of ash pit used where the slag is drawn off in the molten state, particularly regarding the relative dimensions of a furnace of that kind, in order to keep the ash in a molten state and not have it become chilled and hardened in the ash pit; also, must the ash be kept closer to the hot zone, to the flame, than under ordinary conditions.

R. J. S. PIGOTT (Smoot Engineering Corporation, New York, N. Y.): It appears from the several papers that have been offered on this subject that there is as yet no clear decision as to whether we want the ash to come out of the furnace dry or wet. Some points appear clear, however; one being this. If the boiler is to be kept clean over long periods, requiring little dusting and forming little accumulation of slag on the tubes, the maximum ash fusion temperature coal is probably desirable; or else a large cooling surface and a low rate of B.t.u. release per cubic foot.

If a low fusion ash coal is used, it means a very large furnace, a much larger amount of cooling to keep the boiler clean. However the thought of reducing the size and the cost of the furnace by running to a higher furnace temperature offers considerable attraction. This usually implies that the boiler proper must either be increased in size, or must give a higher flue temperature, because it is perfectly obvious that if the furnace is kept hotter the boiler surface itself will have more to do. The question becomes one of whether you prefer to pay for surface in the furnace-walls or in the boiler.

It looks as though we would ultimately come to slag removal, but with the process of heat development in a hot furnace separated from the process of heat absorption. Certainly, the fine, dry ash produced by the powdered coal furnace is a nuisance from every quarter. It has no particular commercial value at present. It is very hard to wet, even to remove in a sluice, and a great deal of it goes up the stack and has to be taken out by some kind of a dust eliminator, none of which have been a complete economic success as yet. The dust eliminators offering high percentage of removal are very expensive and bulky.

Recently the writer had the opportunity to lay out a new design of furnace for stokers at Kearny Station. We finally decided to cool the furnace completely. This is one of the earliest installations in which a complete bare-wall design was put in for under-feed stokers. A good deal of fear was expressed that these furnaces would smoke badly because it was reported that in Richmond Station some difficulty was experienced in a rather completely cooled furnace, until the operator found out how to handle the fires under those conditions. In the limited operation so far at Kearny, there has been shown no more tendency to smoke than with a complete refractory-wall furnace. The walls remain absolutely clean. So far, the only accumulation noticed

after a month's operation with ratings up to 300 per cent, is a thin film of white or gray dust. There are no clinker accumulations anywhere about the

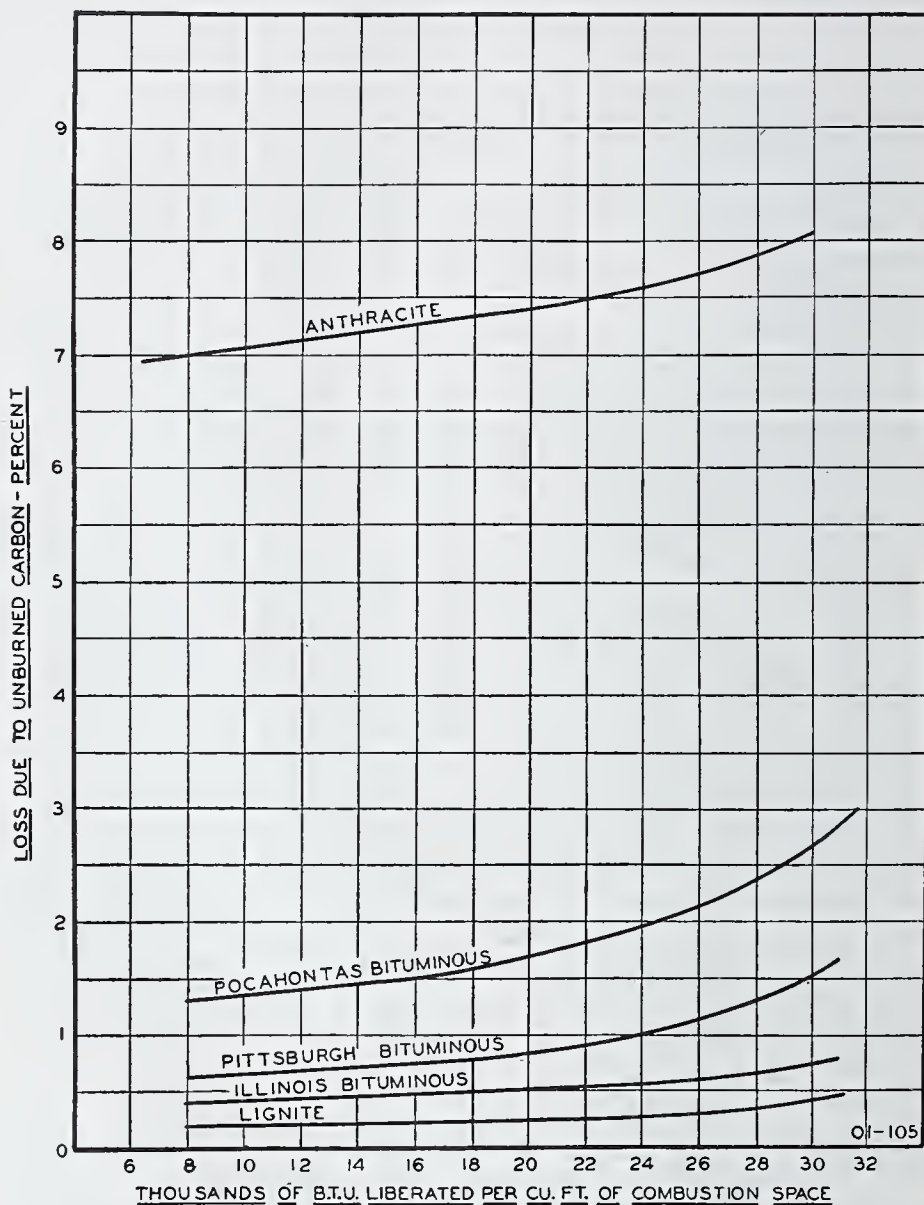


FIG. 1. LOSS ATTRIBUTABLE TO UNBURNED CARBON IN FLUE DUST DEPENDS ON ORIGIN OF COAL

boiler and there is hardly any slag accumulation on the tubes. The bare wall is protected with cast-iron blocks for a space of about three feet above the

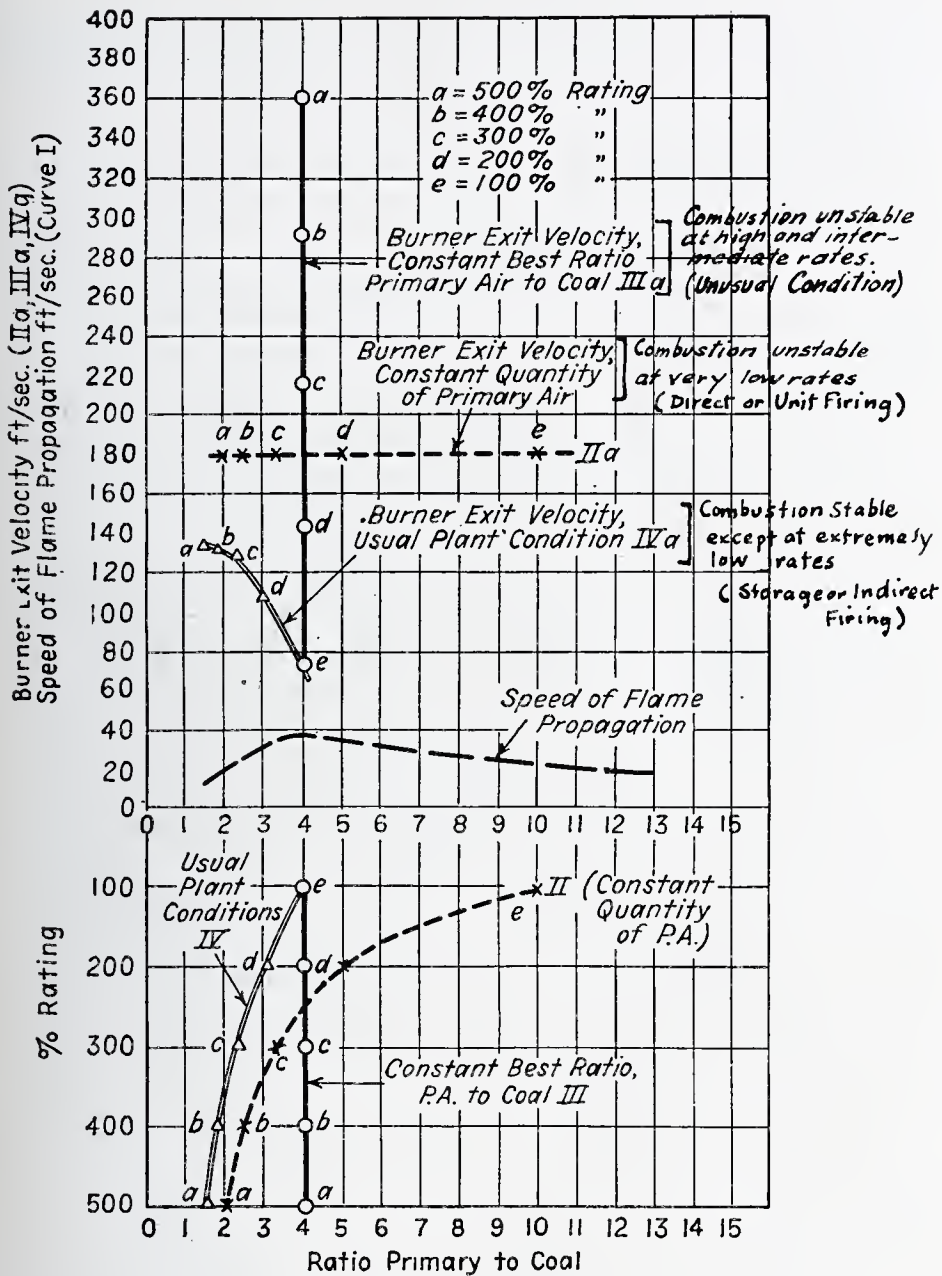


FIG. 2. COMBUSTION MAY BE UNSTABLE AT HIGH AS WELL AS LOW RATES DEPENDING ON RELATION BETWEEN VELOCITY OF FUEL MIXTURE AND VELOCITY OF FLAME PROPAGATION

Curves show characteristics of burners with fuel nozzles of constant size irrespective of combustion rate.

stoker tuyeres in order to avoid too great a heat reduction at this point, and abrasion of the tubes. The water-walls are carried up in open spacing to the top of the boiler, giving approximately one-half per cent additional absorption, providing a 9-inch wall throughout and eliminating buckstays.

A. F. KUNBERGER (United Gas Improvement Company, Philadelphia, Pa.): When Dr. Bunte showed the second curve, he mentioned that between the softening point and the melting point the original curve showed a zig-zag formation rather than a straight line. Dr. Bunte mentioned that this was due to the formation of phosphoric acid. I would like to know whether the effect produced was due to the formation of phosphoric acid or to the evolution of phosphoric acid?

MARTIN FRISCH (Combustion Engineering Corporation, New York, N. Y.): In their excellent discussion of the effects of various factors on the amount of unburned carbon in the flue dust the authors barely alluded to the effect of the nature of the coal. It does not seem that this factor was given the prominence that it deserves. The nature of the coal has probably more to do with the amount of unburned carbon in the flue dust than any other factor mentioned in the paper. Test data collected during the past several years indicate that with a given type of combustion equipment, i.e., with a given method of producing turbulence, the carbon loss increases as the geologic age of the pulverized coal used increases. Figure 2 based on experimental data shows this. Lignite, which was formed more recently than the coals we burn, most closely resembles wood and other vegetable matter and may be burned in pulverized form almost completely down to an ash which is but little contaminated with unburned carbon. The sub-bituminous coals and the better western coals of the free-burning non-coking type such as Illinois coal may also be burned with small loss of unburned carbon in the ash and flue dust, though the loss is greater than with lignites. As we consider in turn Pittsburgh, Pocahontas, and finally anthracite coal in the order of their ages we find that the loss becomes greater and greater. In short, the loss may be a fraction of one per cent when burning lignite and eight per cent when burning anthracite.

The rapidity of combustion may depend either on physical or chemical factors peculiar to the coal. Particles of some coals grow larger and other coals smaller during the combustion process.

Coking coals become soft when heated and the particles tend to fuse together into clusters. Collisions between small particles while in the plastic stage aid this process and cause larger particles to result from the fusion of the smaller ones, which present relatively less surface for contact with oxygen and so do not burn as fast. Evidence of this is found in the flue dust of coking coals where coke particles considerably larger in mass and volume than the particles of coal originally fed to the furnace are often found.

Particles of free-burning coal do not become sticky when heated and do not fuse together. Such particles give off a great deal of volatile which burns readily so that a comparatively small amount of the combustible needs to be burned as fixed carbon. Particles of sub-bituminous coals, and of lignites especially, disintegrate into smaller particles instead of fusing into larger

pieces. The particles in effect undergo further pulverization while burning and a great deal of extra surface is exposed for the action of oxygen so that the fixed carbon burns readily.

Anthracite coal is the most difficult to burn in pulverized form because the anthracite particles are dense and contain relatively more combustible for a given amount of exposed surface than the softer coals and the low grade of solid fuels. The combustible is almost entirely fixed carbon and its combustion can take place only as fast as oxygen can come into contact with the surface of this particle.

The chemical reactivity of the fixed carbon in various coals with oxygen also differs with the physical characteristics of the various coals and hence the completeness of combustion in the time available also differs. When oxygen unites with the carbon of coking coals the immediate products may contain little carbon monoxide. When the fixed carbon of lignites (and perhaps of the free-burning coals to a lesser extent) burns the immediate products contain considerable carbon monoxide which readily finds the small amount of oxygen needed to burn it to carbon dioxide after diffusing into the furnace atmosphere. It is evident why lignites and free-burning coals are easier to burn completely in pulverized form, than coking coals. Thus we see that Figure 1 has both a physical and chemical explanation and great variations in the completeness with which various coals may be burned in a given time with a given equipment must be expected. These variations are generally greater than those produced by the usual factors considered. Consequently when changes in furnace efficiency are studied it is very important to first find out to what extent a change in fuel can account for these before investigating the effects of changes in the equipment or in the process.

The paper seems to ascribe considerable importance to the influence of furnace temperature on the carbon loss and concludes that the stability, speed and completeness of combustion depend largely on the furnace temperature. Unstable ignition usually experienced at low combustion rates was cited as evidence of this. It is undoubtedly true that considerable difficulty is sometimes experienced in maintaining combustion at low rates with burners of large capacity. But this may be correctly explained on the basis of factors that have nothing to do with the furnace temperature. The explanation may be verified by experiment. Inflammability of pulverized coal depends on its physical and chemical properties, its fineness and on the ratio of primary air to coal in the fuel mixture. The velocity of flame propagation through each mixture is peculiar to that mixture. If the mixture is introduced into a furnace with a velocity that is too high ignition will take place too far from the burner. The velocity can be so high that by the time the speed of the mixture has decreased to the velocity of flame propagation the jet has spread out and thinned out to such an extent that the particles of coal are either too far apart for flame propagation or because of segregation the ratio of air to coal at any given location may vary so widely from instant to instant that the flame shifts back and forth along the jet and from place to place in the furnace. This may and often does cause pulsations. If the inflammable zones get too far apart the propagation of flame may be retarded and the fire may snuff out. This phenomenon often occurs at very low rates of combustion and because at

those times the furnace is usually cold it has been customary to deduce that the low furnace temperature is to blame for the unstable combustion. But the same phenomenon may be reproduced at high rates of combustion with a hot furnace. And, conversely, as has been often demonstrated, very small amounts of pulverized coal may be burned in very large and relatively cold furnaces—even out of doors—if the burner is of such design that the velocity of the fuel and the ratio of air to coal may be properly controlled.

Burners are usually designed for high combustion rates and most commercial types have a capacity range of 1 to 4. Many have a range of only 1 to 2. Some few are more flexible. Few burners are suited for both very high and very low capacities. The oil burner people have had the same experience and for this reason they use a large number of burners of relatively small capacity per furnace. They have no trouble in keeping a single burner in efficient operation though at maximum demand twelve such burners might be in use in the same furnace. Powdered coal users are confronted with the same problem, which for them is more difficult because of the difficulty of subdividing a mixture of powdered coal between a large number of burners. Therefore fewer burners of large capacity must of necessity be used when direct firing is employed and it is with direct firing chiefly that there is trouble in operating at low combustion rates. The explanation for this is found in the fact that in general for a given pulverizer the quantity of primary air mixed with the fuel delivered to the burners is practically constant irrespective of the amount of fuel. This limitation is imposed by the pulverization process and also by the piping and burners in which the velocity must always exceed a certain minimum so that coal may not settle out. Consequently at low combustion rates the ratio of primary air to coal is high, the velocity of flame propagation low and the jet velocity of the fuel mixture is almost, if not quite, as high as at high combustion rates. As a result ignition may take hold at some distance from the burner and may flicker to and fro in an unstable manner. Study Figure 2 and the explanation becomes simple.

It is possible although it may not always be practicable to design burners so that ignition at low rates of combustion may be just as stable and combustion just as efficient and compete as at high rates. A candle may be burned outdoors or in a room, or in a furnace with absolutely cold walls. The same is true of a very small gas flame or an oil flame or a powdered coal flame, if the burner is designed to accomplish this. The temperature of the surrounding is not all important. As a matter of fact the temperature is the effect and not the cause of combustion.

Mr. Bailey and Dr. Jacobus in their paper also reached the interesting conclusion that there is considerable segregation of the various constituents of the ash originally in the coal. This is based on the fact that samples of ash from some of the coal found at various points of the furnace, boiler, and other points of the setting were found to have different melting points. Dr. Bunte on the other hand presented a paper devoted to the study of the effect of the combustion process on the properties of coal ash and he concludes that samples of ash of a given coal found in different points of the setting had very nearly the same melting point although their softening points might differ to some extent. In view of these conflicting conclusions one is led to suspect

that the melting point test method may have something to do with the results reported. Dr. Bunte's method differed materially from the method employed by the authors. A standardization of the melting point test methods seems to be needed in order that results given by different authors may be compared and such conflicting conclusions avoided. At any rate it seems to be unsafe to generalize about the segregation of the combustible in coal ash at this stage of the game. Segregation may be a fact for some coals and not for others.

GEO. A. ORROK: It has been a great pleasure to listen to these three papers today, and to learn a little more about ash and its fusion point, particularly about the amounts we are wasting in our stacks.

A number of years ago I made an investigation as to the amount of unburned coal and ash that went up a household chimney. I was led to this investigation by reading of some work that had been done in England in a substantially similar manner. A sampler inserted in the household chimney, connected to an aspirator soon collected a sufficient amount of material to weigh. I discovered in my own chimney about 2.5 per cent by weight of coal was going up the stack. The reports from England were a trifle higher than that and were figured at about 3 per cent. I think you will find these in the old report of the Smoke Commission in 1893.

If we are turning out of our household chimneys in soot, ash, and unburned coal between 2.5 per cent and 3 per cent of the coal that we burn in household heating apparatus, you can see that the work done in the power stations by the use of cinder catchers in reducing this amount to under one-half of one per cent of the coal is a remarkable addition to the cleanliness of our atmospheres.

In the city of New York, for instance, where 18,000,000 tons of coal are burned every year, if we had our old systems of household heating and 3 per cent of the coal went up the chimneys, that would be quite an amount of dust to scatter over the area of New York, but with probably 60 to 70 per cent of this coal burned in power stations and large installations where the dust can be kept down, the amount of dust spread over the city with our 18,000,000 tons probably does not amount to more than, say, one-sixth of the amount that would have been spread under the old method of handling the heating of the city.

DR. BUNTE: In answering Mr. Kunberger regarding the formation of phosphoric acid, I think there are two cases. It is possible there is a reaction between the phosphate and some other compound of the ash. This would happen immediately, or perhaps later in some cases. It is possible that there is phosphate to decompose. The decomposition, I think, must be at one temperature. Therefore, I think there would be a reaction between any silicate, or any other substance with phosphate, which takes place over the whole melting process. We hope to find this out by testing with clean materials.

MR. ORROK: I would like to ask just one question more. I understand, although I may be mistaken, that the author refers to phosphoric acid in the ash. If that is so, where does it come from? Do you take it out of the air, or where?

DR. BUNTE: Phosphate.

MR. ORROK: How can you find phosphoric acid in the ash from coal?

MR. BAILEY: Mr. Orrok has raised a question of how can you find phosphate in coal. Some twenty years ago I was with one of the larger coal companies selling a good deal of coal to by-product ovens. One of our customers wanted to know what the phosphorus in our coal was. Our chief inspector came to see him and found the percentage was down to about 0.4 per cent.

MR. ORROK: I get about one-hundredth of one per cent phosphorus which is about the average in American coal. There are a few coals that run higher, but very, very few.

MR. BAILEY: Answering Mr. Andrew's question about the dimensions of the slag tap furnace, and other features of its construction, we have used several different sizes. At Buffalo the first furnace was 8 feet square. Three furnaces which shortly followed were 16 feet square. The four boilers installed this year were  $18\frac{1}{2}$  feet square. These dimensions all apply at the slag level. These furnaces are each a little larger where they enter the boiler pass. There are some other furnaces 22 feet square and one now being installed 20 by 34 feet. As to the area of the furnace, I do not believe that it is a limiting factor. It is largely a matter of temperature in the furnace and the fusing temperature of the ash in the coal, or that portion of the ash which accumulates in the bottom of the furnace. It is noted from Figure 15 that there is a segregation of ash resulting in a material of lower fusing temperature accumulating in the bottom of the furnace.

This type of furnace makes an ideal arrangement for horizontal firing with the hot portion of the furnace at the bottom and the burners can be directed against the slag bottom which makes a very good target wall for mixing the fuel and the air. This enables any coarse particles of coal to be readily burned when floating on the molten slag.

With reasonable rates of combustion up to 15,000 or 20,000 B.t.u. per cubic foot there is no difficulty in handling coal with a fusing temperature up to 2,500°F.

The construction of the furnace is very simple. The side walls should be water-cooled with the proper protection of the tubes at this level. It is common knowledge that in glass furnaces and heating furnaces the erosion of the walls is greatest at the slag line and very little trouble results from the floor, hence a floor consisting of two or three courses of fire brick laid on a steel plate, properly sealed against slag leakage, serves very satisfactorily. There is no indication of any serious maintenance problem in connection with the handling of molten slag.

As Mr. Pigott said, the question before the profession today is, are we going toward dry ash removal, or liquid ash removal. I think the liquid ash removal is more than just a passing fancy. We have been endeavoring to get complete combustion with a minimum of excess air, which means high furnace temperatures. To do that in one part of the furnace, and then collect the ash dry and

unfused and cool in the lower part of the furnace, is rather a difficult problem, and it has not always been done successfully. The slag tap furnace fits in very well with high rates of combustion and lower excess air, which gives high temperatures or high heat potentials, which are analogous to high steam pressures and high voltage electric current, all of which seem prevalent among modern engineering progress.

As to Mr. Frisch's question, the curve showing different kinds of coal brought out quite clearly the higher carbon loss from anthracite under the same rates of combustion, but few data here presented from semi-bituminous coal indicate the carbon loss somewhere between that from the anthracite and bituminous, all of which coincides with Mr. Frisch's comments, although the relative position of these curves does not quite agree with the paper presented at the World Power Conference in London a few weeks ago.

As to the difference between Pittsburgh coal and Illinois coal, Figure 3 gives data from both coals in the same furnace, at the same rating, from which data there does not seem to be any material difference in carbon loss. Most of the data and conclusions reached in regard to fineness and other factors were quite comparable because they relate to high volatile coals with perhaps a slight difference in their coking properties.

It is very evident from the data presented with variations in fineness with the same coal in the same furnace, that such factors as fineness, furnace temperature and excess air do influence the carbon loss.

As to low ratings, there is a limit beyond which fuel can be burned due to a low furnace temperature. That has been brought out quite strongly in connection with the Scotch marine furnace, where carbon loss is considerably higher than on a furnace with brick walls.

Mr. Frisch compares the burning of pulverized coal with the burning of a candle. This is not quite a true analogy. I only wish pulverized coal was as easy to burn as is a candle.

The segregation of ash and its fusing temperature may be partly due to the method of determining the fusing point. I appreciate the method which has been described this afternoon by Dr. Bunte. I think more attention should be given to methods of determining the fusing point and its complicated effect upon different factors. The fusing point alone does not tell you very much. We must find out just what are the characteristics of fluidity, or non-fluidity or ash, and segregation, in various forms as we handle it through our furnace. I think, however, an effort should be made to work upon the principle of minimizing the dust nuisance as much as possible by collecting it in the furnace and this can be done best with a slag tap furnace and having the sticky ash flowing down the furnace walls.

PROFESSOR ESTEP: Mr. Rice has asked me to explain, if possible, the difference between the ash softening temperature as determined by the cone method and that determined by Dr. Bunte's method.

I would explain it in this way. If a cone which has shown some distress upon heating is examined under some magnification it will be found that certain parts have fused and become liquid while other parts have not been affected at all and show no signs of fusion.

The cone does not begin to tip over until the low temperature fusing portion becomes liquid enough to permit the high temperature fusing portion to flow along with it. Hence, there can be considerable softening of certain parts of the cone before the cone shows any distress.

On the other hand, the softening of any part of the specimen used in the Bunte method will be shown on the chart and distress will be indicated at a lower temperature than when the cone is used.

## FUSING POINT OF ASH FROM MIXTURES OF COAL AND FOREIGN MATERIALS

By W. D. LANGTRY AND J. F. KOHOUT

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The following investigation was suggested by the number of complaints that retailers of coal have been receiving annually concerning the clinkering of coal ash in household and apartment heating equipment, these retailers in turn complaining to the coal operator. Observations have revealed the fact that garbage, and other foreign materials, very often are burned in the fire box with coal, so laboratory tests have been conducted to see what effect the mixing of garbage ash and coal ash would have upon the fusion temperature of the mixtures.

To the best of our knowledge, the householder in the United States consumes about 16 per cent of the entire output of coal in the country and yet this small percentage is one of the biggest factors in public opinion, so that when they have complaints that affect the home it becomes generally known. To this tonnage should be added the coal burned in apartment buildings, which, in the larger cities, house a big portion of the population of the country.

Many complaints from homes and flat buildings regarding the burning of coal have dealt invariably with clinker formation. Investigations have revealed many causes for this condition. One particular phase of clinker formation deals with the mixture of garbage and other material decidedly foreign to coal; also the mixture of two or more coals from different fields.

In some communities it is unlawful to dispose of garbage by burning it, so it is wrapped in paper and placed in receptacles in the alley for collection, and then taken to a garbage disposal station. Human inclination, however, is to seek the easiest way to get rid of it, especially during zero weather and inclement days, so the garbage is burned in the stove or furnace.

It is not an uncommon thing to see barrels of garbage in the basement of apartment buildings every morning, that have been collected from the back doors of six, twelve, forty-eight, or sixty apartments. It is not hard to imagine that this conglomerate mass contains everything from the first to last courses of breakfast, lunch,

and dinner; glass bottles of all sizes and descriptions are to be found in greater quantities than ever before. In some cases the glassware and tin cans are picked out; others it is not.

In order to find out at what temperature the ash would fuse from all kinds of refuse rejections from homes, stores, commission houses, hotels, etc., samples were obtained at a large incinerator in a city of about 50,000 inhabitants. It was found that all classes of refuse of a vegetable, animal, and mineral nature consisting of wood, tin cans, boxes, nails, glassware, bones, garbage, paper, etc., were disposed of by burning. An average sample was obtained of the resultant ash and a fusion temperature determination made upon the ash as it was taken from the incinerator. This fusion temperature is reported under laboratory No. 62437 as Sample "A" in Table I which follows. This same sample was then hand picked so that all

TABLE I

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<i>Sample "A" (from large incinerator) consisting of vegetable, animal and mineral refuse</i>	
Lab. No. 62437—fused 2,023°F. (including all refuse)	
Lab. No. 62438—fused 2,140°F. (excluding part of metal and glass)	
<i>Sample "B" (from fertilizer company) consisting of animal and vegetable matters</i>	
Lab. No. 61918—fused 2862°F.	
<i>Sample "C" (household garbage)</i>	
Lab. No. 62208—fused 2,090°F. (vegetable matter exclusively)	
Lab. No. 62394—fused 2,480°F. (vegetable and animal matter)	
Lab. No. 62491—fused 2,665°F. (vegetable and animal matter)	

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visible pieces of glass and metal material were eliminated and then a fusion temperature made upon it and listed herein under laboratory No. 62438, also shown in Table I.

Likewise, a sample of garbage was secured from a large fertilizer company which collected the garbage from big hotels. This consisted only of the refuse from the kitchens and dining rooms made up of vegetable and animal matter, and was pressed into large cakes from which were taken the samples and these then burned to ash, the fusion temperature of which is reported above as Sample "B" in Table I.

Garbage of strictly vegetable nature, i.e., exclusive of meats, bones and mineral matter, was secured from the ordinary household table and burned to ash, the fusion temperature being reported as Sample "C," in Table I.

TABLE II

MIXTURES OF DIFFERENT PERCENTAGES OF COAL AND GARBAGE ASH TO SHOW  
EFFECT ON FUSION TEMPERATURE OF MIXTURES

PER CENT OF MIXTURE		LABORA- TORY NUMBER	FUSION OF INDIVID- UAL SAMPLES	COMPOSITE OF COAL AND GARBAGE ASH FOR FUSION
Example "A"				
90	Semi-bituminous coal ash	61648	2,567	} 2,307
10	Garbage ash	61918	2,862	
75	Same coal as above	61648	}	2,225
25	Same garbage as above	61918		
50	Same coal as above	61648	}	2,420
50	Same garbage as above	61918		
Example "B"				
90	Semi-bituminous coal ash	61649	2,567	} 2,310
10	Garbage ash	61918	2,862	
75	Same coal as above	61649	}	2,225
25	Same garbage as above	61918		
50	Same coal as above	61649	}	2,390
50	Same garbage as above	61918		
Example "C"				
90	Semi-bituminous coal ash	61650	2,691	} 2,252
10	Garbage ash	61918	2,862	
75	Same coal as above	61650	}	2,290
25	Same garbage as above	61918		
50	Same coal as above	61650	}	2,390
50	Same garbage as above	61918		
Example "D"				
90	Semi-bituminous coal ash	61718	2,539	} 2,185
10	Garbage ash	61918	2,862	
75	Same coal as above	61718	}	2,214
25	Same garbage as above	61918		
50	Same coal as above	61718	}	2,375
50	Same garbage as above	61918		

TABLE II—*Continued*

PER CENT OF MIXTURE		LABORA- TORY NUMBER	FUSION OF INDIVID- UAL SAMPLES	COMPOSITE OF COAL AND GARBAGE ASH FOR FUSION
Example "E"				
90	Eastern bituminous coal ash	61959	°F. 2,525	} 2,201
10	Garbage ash	61918	2,862	
75	Same coal as above	61959	}	2,278
25	Same garbage as above	61918		
50	Same coal as above	61959	}	2,375
50	Same garbage as above	61918		

It will be seen in Table I that there is a marked difference in the fusion temperature of the resultant ash of garbage and refuse from 2,023° to 2,862°F. This indicates that there is a wide difference in the temperature at which refuse of this nature will fuse, it all depending upon its general make-up.

In order to see what effect this kind of refuse would have upon the clinkering property of coal ash, mixtures of varying proportions of coal ash and the resultant ash from garbage in all of its forms were made up and the fusion temperatures of the mixtures determined. These results are shown in Table II.

It is plain to be seen from the tabulations that the admixture of garbage ash with coal ash caused a lowering of the fusion temperature of the coal ash. This is particularly noticeable in the case of the garbage ash, laboratory No. 61918, which fused at 2,862°F., this being a very high fusion temperature in itself, but when mixed on a percentage basis with coal, it reduced the fusion temperature of all coal ashes with which it was mixed.

It would be reasonable to assume that if even a smaller percentage of garbage ash were mixed with coal, the fusion temperature might even be lowered to a greater extent.

The foregoing article takes into consideration only one phase of the admixture of foreign material with coal. In other research work which will be carried on by us during the coming year, additional information will be obtained as to the mixing of different coals and fuels together on different percentage bases.

TABLE III

MIXTURE OF COAL AND GARBAGE ASH ON A PERCENTAGE OF 90 PER CENT COAL  
AND 10 PER CENT GARBAGE ASH

PER CENT OF MIXTURE		LABORA- TORY NUMBER	FUSION OF INDIVID- UAL SAMPLES	COMPOSITE OF COAL AND GARBAGE ASH FOR FUSION
			°F.	°F.
90	Western bituminous coal ash	62035	1,946	} 1,862
10	Garbage ash	61918	2,862	
90	Eastern bituminous coal ash	62037	3,000	} 2,665
10	Garbage ash	61918	2,862	
90	Western bituminous coal ash	62246	2,130	} 2,081
10	Garbage ash	62208	2,090	
90	Eastern bituminous coal ash	62479	2,946	} 2,450
10	Garbage ash	62394	2,480	
90	Eastern bituminous coal ash	62479	2,946	} 2,341
10	Refuse from incinerator	62437	2,023	
90	Eastern bituminous coal ash	62479	2,946	} 2,324
10	Refuse from incinerator	62438	2,140	
90	Western bituminous coal ash	62482	2,185	} 2,193
10	Garbage ash	62394	2,480	
90	Western bituminous coal ash	62482	2,185	} 2,185
10	Refuse from incinerator	62437	2,023	
90	Western bituminous coal ash	62482	2,185	} 2,158
10	Refuse from incinerator	62438	2,140	
90	Eastern bituminous coal ash	63436	2,678	} 2,294
10	Garbage ash	61918	2,862	
90	Eastern bituminous coal ash	63436	2,678	} 2,225
10	Garbage ash	62208	2,090	
90	Eastern bituminous coal ash	63436	2,678	} 2,270
10	Garbage ash	62394	2,480	
90	Eastern bituminous coal ash	63436	2,678	} 2,334
10	Refuse from incinerator	62437	2,023	

TABLE III—*Continued*

PER CENT OF MIXTURE		LABORA- TORY NUMBER	FUSION OF INDIVID- UAL SAMPLES	COMPOSITE OF COAL AND GARBAGE ASH FOR FUSION
			°F.	°F.
90	Eastern bituminous coal ash	63436	2,678	} 2,278
10	Refuse from incinerator	62438	2,140	
90	Eastern bituminous coal ash	63436	2,678	} 2,302
10	Garbage ash	62491	2,665	
90	Eastern bituminous coal ash	63513	2,405	} 2,271
10	Garbage ash	61918	2,862	
90	Eastern bituminous coal ash	63513	2,405	} 2,290
10	Garbage ash	62208	2,090	
90	Eastern bituminous coal ash	63513	2,405	} 2,341
10	Garbage ash	62394	2,480	
90	Eastern bituminous coal ash	63513	2,405	} 2,375
10	Refuse from incinerator	62437	2,023	
90	Eastern bituminous coal ash	63513	2,405	} 2,358
10	Refuse from incinerator	62438	2,140	
90	Eastern bituminous coal ash	63513	2,405	} 2,324
10	Garbage ash	62491	2,665	

## COKE-BURNING DOMESTIC BOILER

By DR. CHARLES W. BRABBÉE

*Director, Institute of Thermal Research, Yonkers, N. Y.*

Gas consumption in this country is rapidly increasing, and with it the production of coke, which calls for an extensive and economical use for this fuel. In studying any question like this, it is both advisable and profitable to consider first the world-wide developments on the subject and then start the new investigation from the level already reached by our fellow-workers.

European engineers have used coke for a long time as domestic fuel, to their entire satisfaction, and it was really surprising to learn that in the United States coke is used but comparatively little for that purpose. One of the main reasons for this is to be found in the fact that coke needs a very large fuel magazine—almost twice as large as that required for anthracite, if, with the same boiler load, the same length of firing period is to be obtained.

You may therefore be interested in a new domestic boiler which is especially designed to burn coke successfully, in which construction all the European knowledge is used, and a few other promising features have been added.

We see first (Fig. 1), a large, all-sides water cooled magazine  $M$ , so determined that at full rate an eight-hour firing period is guaranteed, which means that the boiler, installed with 25 per cent reserve for pipe losses and 25 per cent reserve for emergency, will call for attention, in average winter weather, not more than twice in 24 hours. We see, further, the desire to use the radiation of the incandescent fuel bed  $R$  as much as possible, a factor which saves iron. At the hottest point  $P$ , secondary air  $S$ , is introduced and the flue gases of complete combustion are then forced through a long revertible travel  $F$  into the collecting smokehood  $H$ , which arrangement assures a highly effective heat transmission by convection. A bypass  $B$  which permits the elimination of the revertible flue and connects the combustion chamber direct with the smokehood, will be discussed later on. An insert piece  $J$  acts as an effective water separator in each section and forces the steam to enter the nipple from the top, which secures dry steam. The performance curve (Fig. 2) of this magazine boiler shows an efficiency of 75 per cent or better, between 25 and 100 per

cent load and the curve is very flat, which means that the boiler is operating economically during all the heating season.

The stack gas temperature at full rate does not exceed 700°F. and the required draft for that load is only 0.22 inch water column. As this boiler is built sideways, whereby each section is a complete boiler

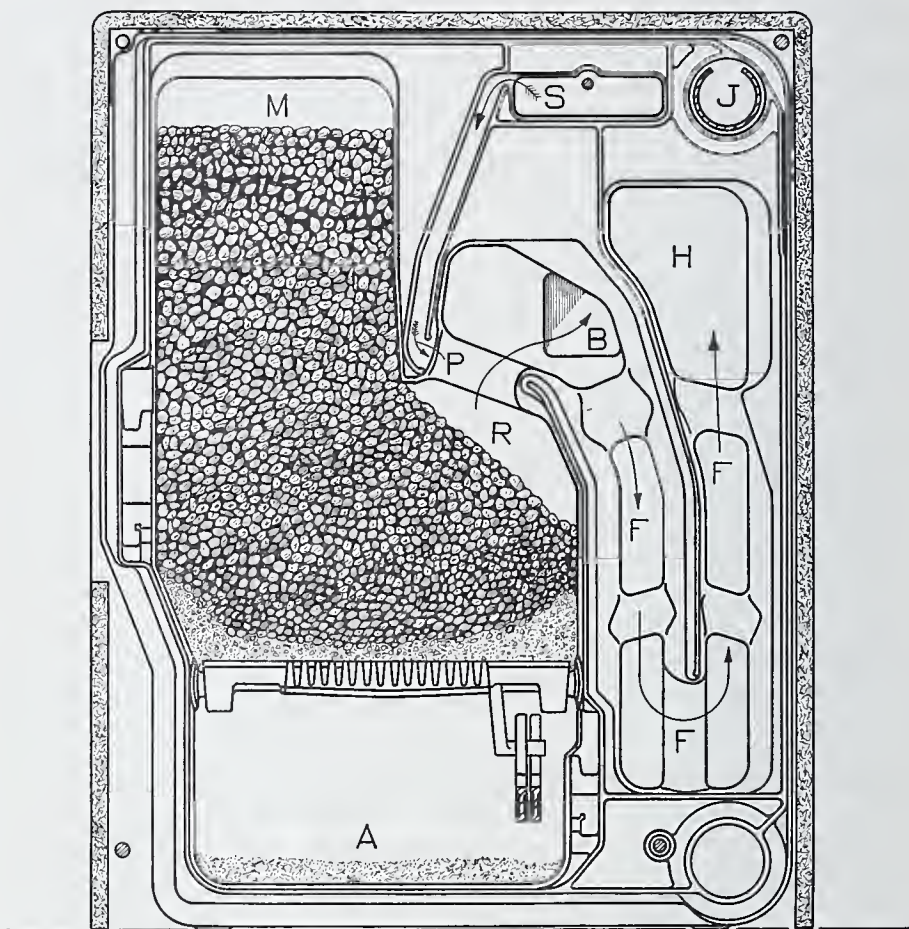


FIG. 1. MAGAZINE BOILER "25" FOR COKE OR STOVE ANTHRACITE (CROSS-SECTION)

in itself, so that live and dead grate, primary and secondary air, heating surface, etc., increase in proportion to the number of sections used, the charts are good for all assemblages—a fact proven by tests.

We also see in Figure 1 a one-way flue travel, a distinct change from European practice, and giving many advantages in weight and space requirements. The boiler has a water-cooled, air-tight ashpit A,

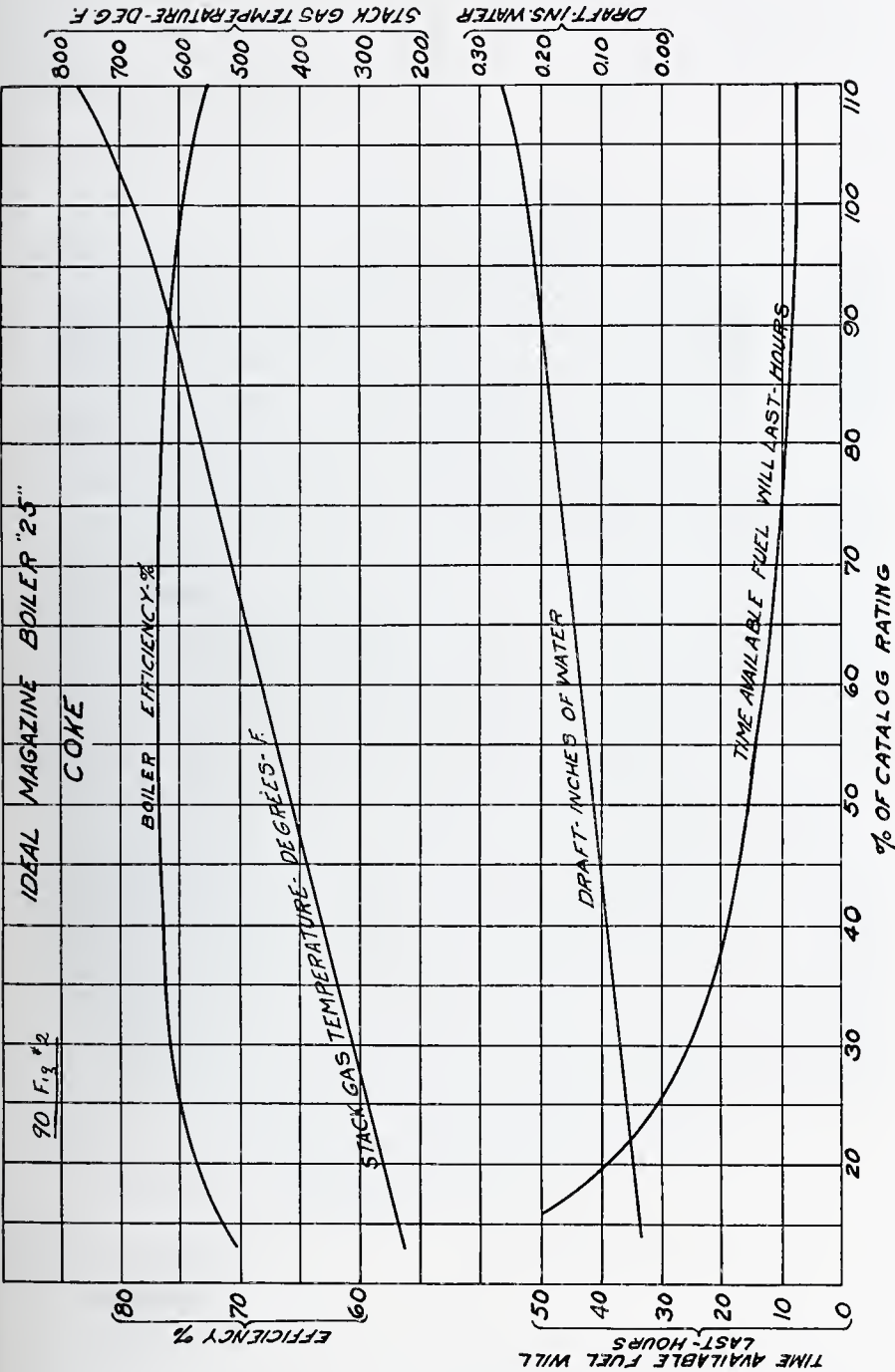


FIG. 2. PERFORMANCE CURVES OF MAGAZINE BOILER "25" WITH COKE AS FUEL

which assures accurate and positive control by automatic regulation. In starting the fire in bad weather, a handle (Fig. 3) is turned to the left side, thereby, as previously mentioned, connecting the combustion chamber directly to the smokehood, which arrangement has given

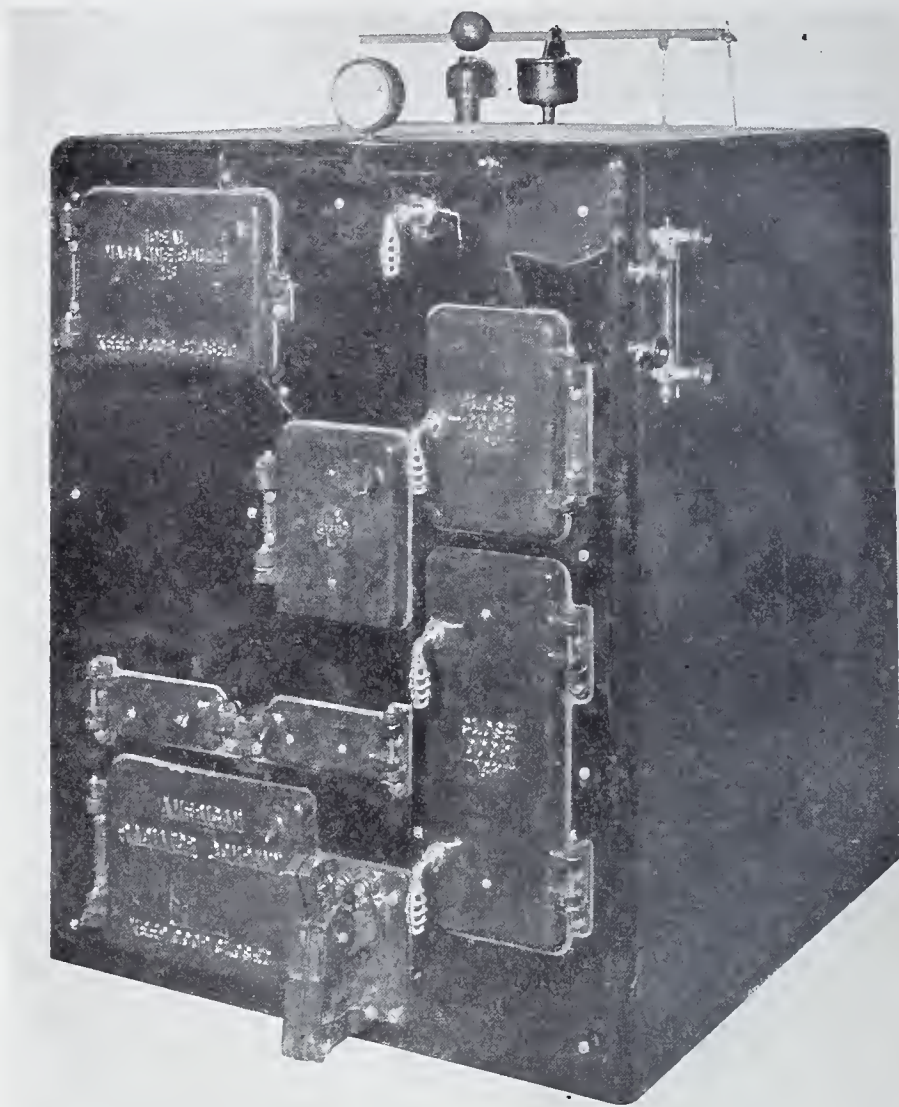


FIG. 3. FRONT VIEW OF MAGAZINE BOILER "25"

full satisfaction. Different gas companies have verified the performance curves, by impartial tests, and although it was tried in every way to operate the boiler under the poorest possible conditions, no dangerous gas accumulation in the magazine could be found.

As this seems to be an important point—more so on account of the spacious magazine and the large amount of coal stored, we would like to go into more detail.

First has to be mentioned that the same handle which, on its left turn, operates the bypass, closes, in its movement to the right, the

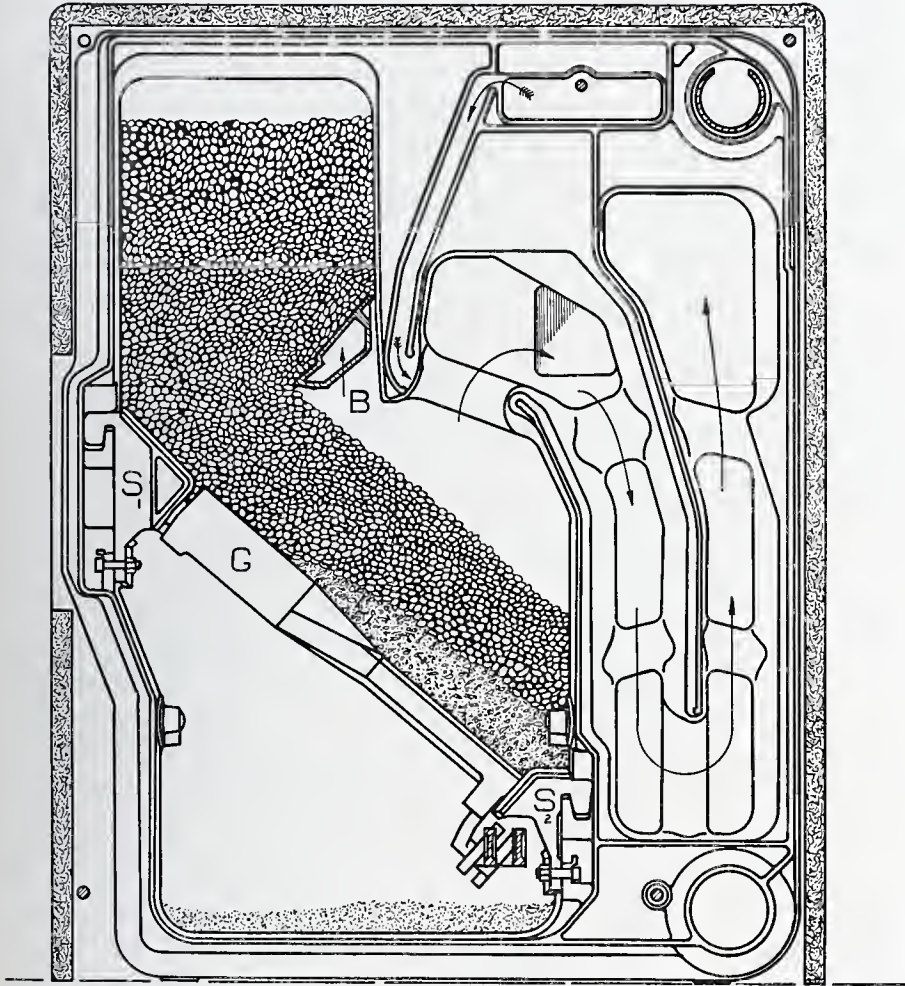


FIG. 4. MAGAZINE BOILER "25" FOR PEACOAAL AND BUCKWHEAT

damper in the smokehood connection to a certain minimum, thereby checking the boiler's output. No separate damper in the smokehood is necessary.

Secondly, we find that in the magazine boiler's feed door, there are invisibly located openings which, by means of the chimney draft, vent the magazine constantly.

To study the effectiveness of these arrangements, the boiler was brought up to full operating load, and then its output suddenly cut

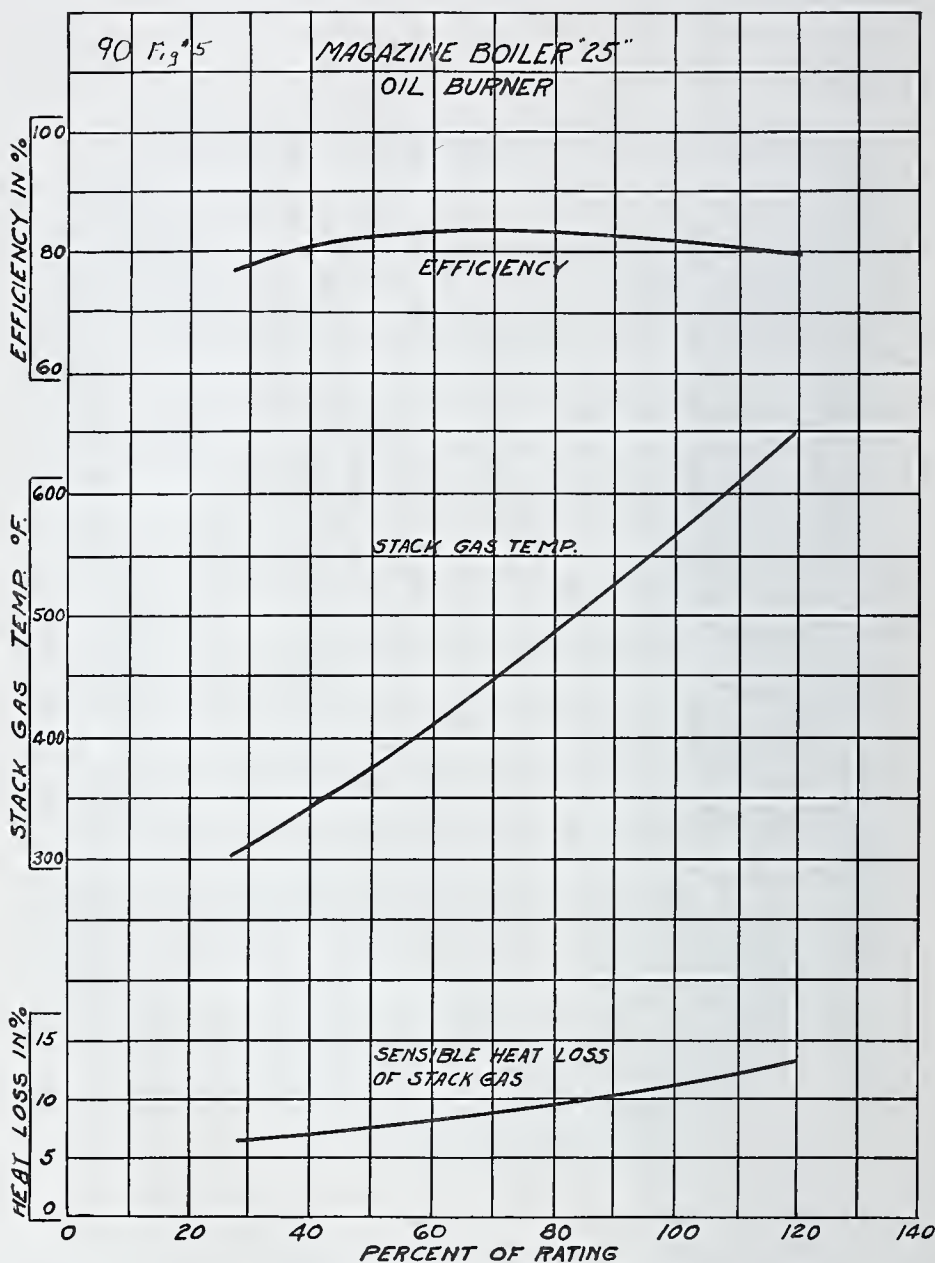


FIG. 5. EFFICIENCY CURVE WITH OIL BURNER

down to 15 per cent of the rating by using the forementioned damper, and by shutting the steam valve which automatically increases the

pressure and forces the regulator to close the air intake and to open the cold air check. The latter is designed in such a way that the cold air enters at the bottom, whereas the hot gases flow on the top of the smokehood, thus making the escape of combustion gases into the room impossible. Under the most unfavorable conditions, the magazine was still under a slightly positive draft, so that no gas could escape into the boiler room. Gas samples taken from the magazine did not show any carbon monoxide, hydrogen, nor methane, and only 0.5 per cent carbon dioxide and 20 per cent oxygen. Similar tests were repeated under likewise severe conditions, and finally everybody agreed that there was no danger with this boiler.

One disadvantage of coke, namely, the necessity of large storage space or the delivery of the year's fuel supply in two or three shipments, cannot, of course, be avoided.

The magazine coke boiler can, without change, be used for the firing of stove or egg anthracite, in which case the performance charts remain about the same, but the firing periods are considerably longer. We emphasize the fact that *good* anthracite is an excellent fuel for this type of boiler. By inserting auxiliary grate supports,  $S_1$  and  $S_2$  (Fig. 4), an inclined specially designed grate  $G$ , and a water-cooled baffle  $B$ , peacoal or buckwheat can be burned satisfactorily in that boiler. An oil burner was also used, and in that connection, the flat efficiency curve at about 82 per cent and above (Fig. 5) with a maximum stack gas temperature of about 570°F. at full rate, speaks for itself.

In our trade there is great confusion at present about how to select the proper boiler size and how to arrange for the necessary boiler reserve, which frequently is taken between 100 and 150 per cent. It therefore may be appropriate to present a little example. Suppose the direct radiation (or its equivalent) which will be installed in the house is 1,000 square feet of steam radiation. Then we figure, under normal conditions, and for the average home, 25 per cent for heat loss of the pipe, and 25 per cent for boiler reserve. For instance:

	<i>square feet</i>
Installed direct radiation.....	1,000
Add 25 per cent for heat loss of pipes.....	250
	1,250
Plus 25 per cent for boiler reserve.....	312
	1,562

The next larger boiler size is an 8-section magazine boiler of 1550 square feet capacity.

For all practical cases, and in connection with the conservative rating of these boilers, the calculation can be still simplified as follows:

	<i>square feet</i>
Direct radiation (or its equivalent).....	1,000
Plus 50 per cent for pipe losses and reserve.....	500
	<u>1,500</u>

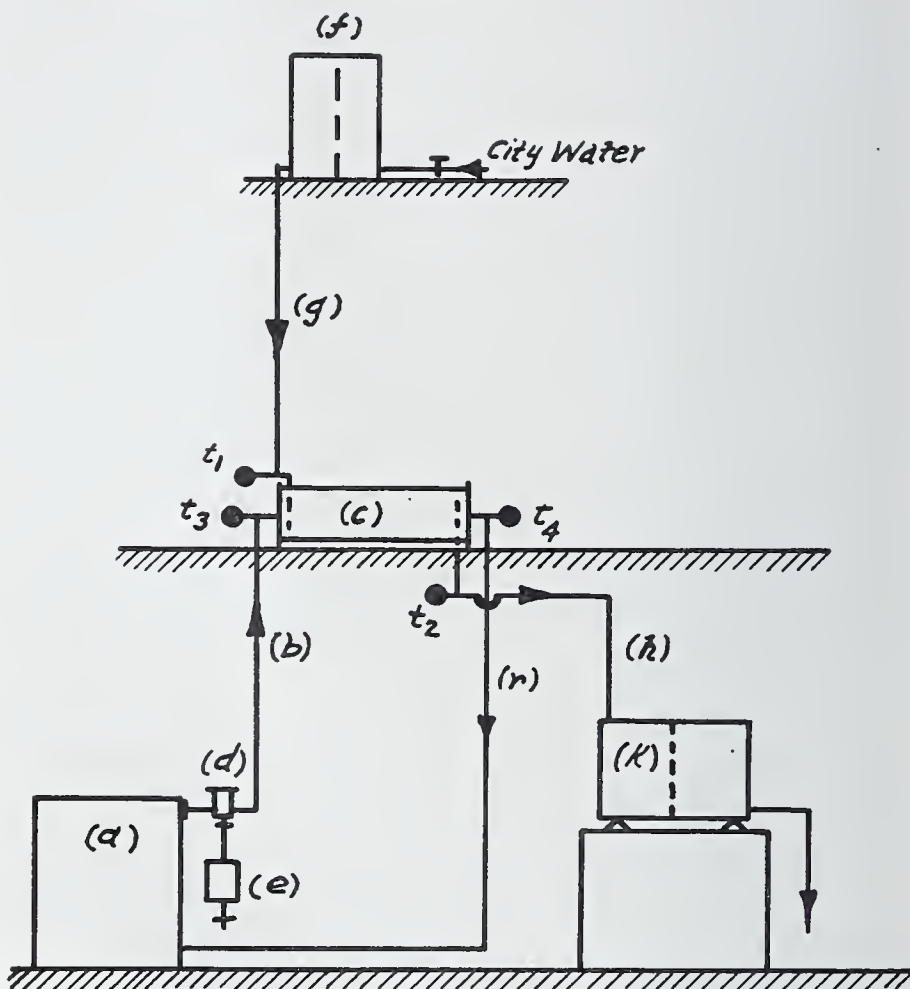


FIG. 6. DIAGRAM OF BOILER TEST EQUIPMENT USED IN THE INSTITUTE OF THERMAL RESEARCH OF THE AMERICAN RADIATOR COMPANY

$a$ , boiler to be tested;  $b$ , flow pipe from boiler to condenser;  $c$ , condenser;  $d$ , water separator;  $e$ , tank to collect the separated water;  $f$ , overflow tank with weirs;  $k$ , dump scale;  $t_1$ , temperature of cooling water entering condenser;  $t_2$ , temperature of cooling water leaving condenser;  $t_3$ , temperature of steam;  $t_4$ , temperature of condensate.

The next larger size is the 8-section boiler with 1550 square feet capacity, which should be selected.

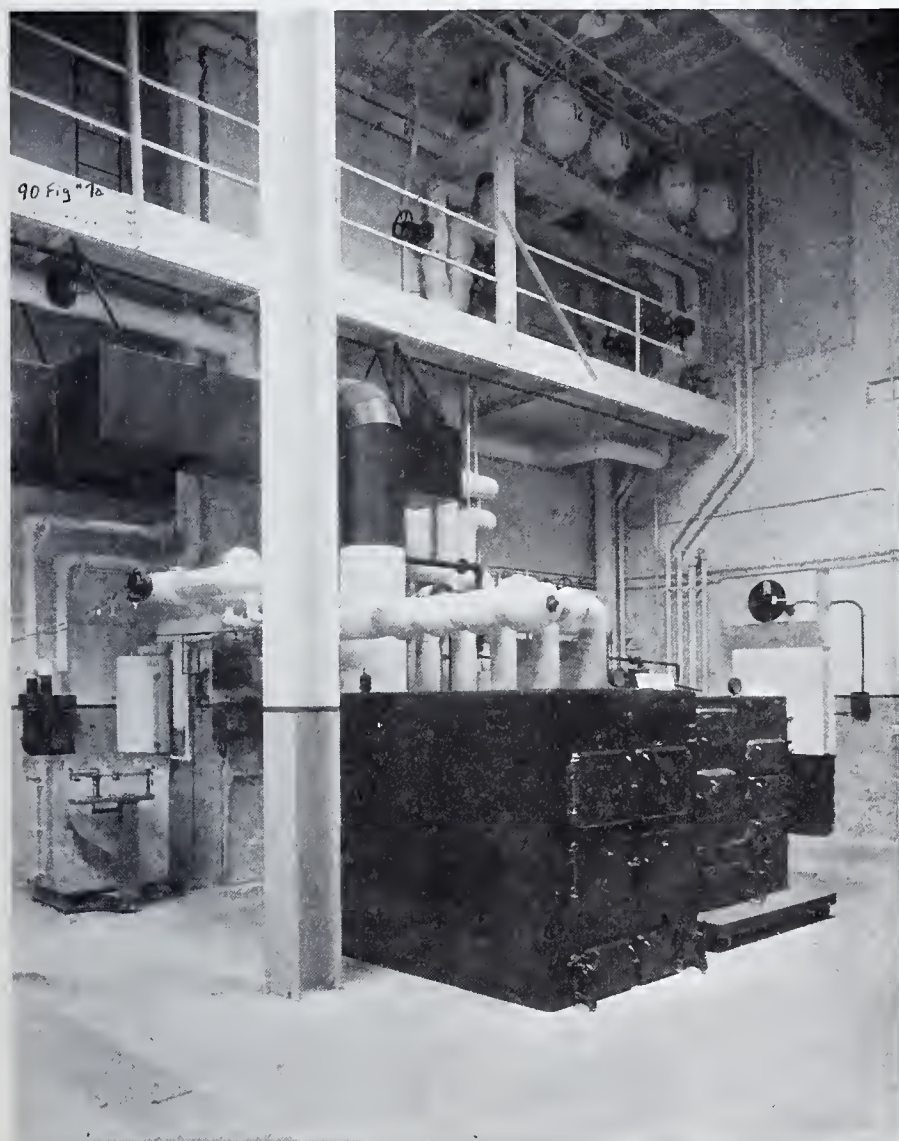


FIG. 7A. BOILER TEST EQUIPMENT FOR BOILER BETWEEN 10,000 AND 30,000 SQUARE FEET STEAM RATING

This meeting is certainly no place to talk about prices of the magazine boilers, but as the price question is usually the first one asked, we would just like to state that the magazine boiler is not more

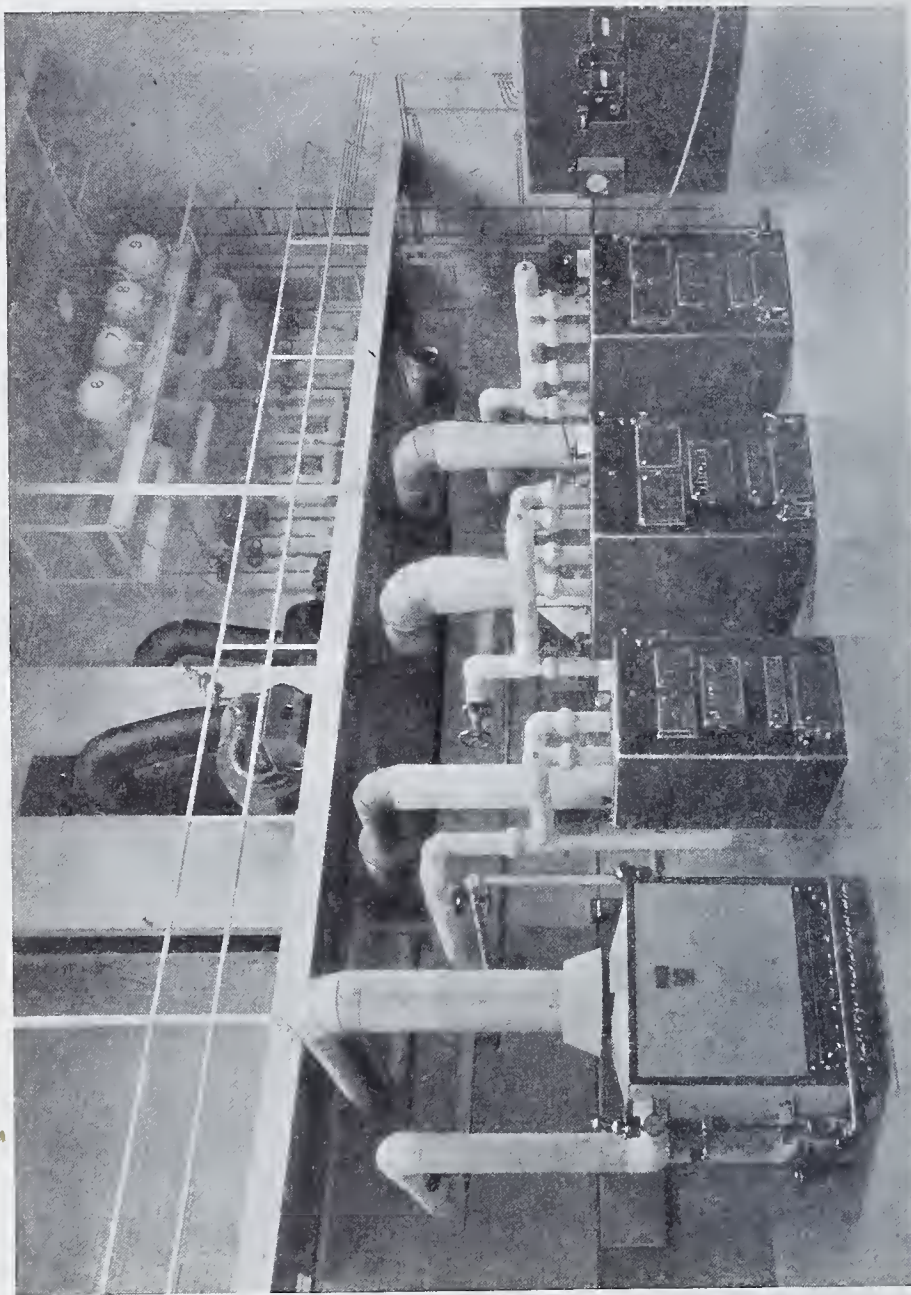


FIG. 7B. BOILER TEST EQUIPMENT FOR BOILERS BETWEEN 2,000 AND 10,000 SQUARE FEET STEAM RATING  
A third equipment for boilers below 2,000 square feet rating is available



FIG. 8. INSTITUTE OF THERMAL RESEARCH, AMERICAN RADIATOR COMPANY, NEW YORK

expensive than any insulated, jacketed and self-feeding magazine boiler on the market. The operating expense of this boiler depends certainly upon the fuel prices, but in general it can be said that this construction, with its high efficiency, its flat efficiency curve, its complete combustion and extremely low stack gas temperature permits considerable savings in fuel costs.

The performance curves referred to, have been obtained with a boiler test equipment (Fig. 6) not usually found in American practice. All steam generated in the boiler (*a*) is delivered to the condenser (*c*), from which all condensate returns to the boiler. The condensation is effected by cold water, the quantity of which and its temperature rise, are observed. As the heat loss of the equipment is known from previous tests, the actual heat output of the boiler can be calculated from the quantity of water and its rise in temperature. This product, divided by the theoretical heat value of the coal burned, gives the direct efficiency of the boiler. On the other hand, Mono readings, stack gas temperatures, and certain other indications, permit the calculation of all heat losses of the boiler, which makes it possible to indirectly determine its efficiency. This method is not only independent of all changes of the conditions of the fire, steam pressure, water line, etc., but works almost automatically and eliminates human error. Each test checks itself, because the direct and indirect efficiency must coincide within reasonable limits. Figures 7a and 7b show part of the boiler test equipment photographed, whereas Figure 8 gives an outside view of our institute, in which also a third boiler test equipment for smaller boilers is available.

# BOILER FURNACES FOR BITUMINOUS COAL

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No element in the process of producing steam from bituminous coal has been developed more rapidly during the last few years than the furnace. Greater capacities, higher efficiencies and better wall materials are among the more important results of this development. While much has already been achieved, the ultimate development of the furnace has not been reached. This paper assumes a knowledge of present-day furnace construction for burning bituminous coal under large boilers with stokers and pulverized fuel. Certain features of these furnaces will be discussed and the probable trend of development will be indicated.

## THE COMBUSTION PROBLEM

The predominating influence of economic considerations in furnace design should be recognized at the start of this discussion. Furnaces that will burn only high grade bituminous coal with ash which fuses above 2300°F., are less difficult to build and less costly than those which will consume low grade coals with ash that fuses at temperatures below 2100°F. When freight rates form a large element in the cost of coal, only the better coals are purchased for the higher boiler efficiency and lower maintenance costs with such coals, make their use more economical than cheaper, low grade coals. The particular design of boiler in use may require a special type of furnace. Engineers in their design of furnaces and selection of the coal to be burned, are governed by "dollar efficiency"; that is the production of the maximum amount of steam for every dollar spent on the total cost of coal, furnace maintenance and fixed charges on the first cost of the plant. Hence it is necessary to consider all these economic phases of the problem when designing a furnace.

Bituminous coal varies widely in composition and these variations require modifications to be made in furnace design in order to secure its best combustion. The moisture content may vary from a small

amount to a large percentage. This variation will effect its rate of ignition on stokers and the extent of drying that will be necessary when used as powdered coal. The ash content is also very variable. The fusing point of the ash has a marked influence on furnace operation controlling clinkering on grates and side walls, and the erosion of brick work by molten ash. Coking and non-coking coals require quite different handling in stokers. Coals which tend to split and dust badly are also troublesome to burn economically on stokers.

The various stages in the combustion of bituminous coal have considerable influence on furnace design. When coal first enters the furnace, any moisture must be dried out. The coal particle then absorbs heat until the gas and volatile matter are evolved. This evolution generally starts at a comparatively low temperature. The gases and vapors distilled, ignite readily and the heat emitted increases the temperature of the remaining coke. While the volatile matter is being evolved, the coal particle is surrounded by an atmosphere of these gases and their products of combustion, and does not come in contact with oxygen until these are swept away. One may therefore assume that air does not reach the coke until the rapid discharge of gases and volatile matter has ceased, unless the air velocity is very high. Hence there must be an appreciable time interval allowed for the combustion of coal. This time required by combustion has a marked influence on the design of furnaces and on the methods employed to burn bituminous coal efficiently. This is particularly true with chain grate stokers where delayed ignition of the coke may cause large quantities of carbon to be carried into the ash-pit. In the case of powdered coal, the length of flame travel or degree of turbulence must be adjusted to provide the proper time for ignition and complete combustion of the coal particle before it enters the boiler tube bank. The relative arrangement of boiler surfaces and furnace walls also has marked effects on the rate of gas evolution and on the ignition of the resultant coke. In the case of stokers, the proper location of arches may greatly accelerate the rate of gaseous evolution and the subsequent ignition of the coke.

The important influence of radiant heat as a means of heat transfer from burning fuel to boiler surfaces, was not fully appraised until within the last few years. This effect is now better understood and all modern furnace designs attempt to take the greatest advantage of radiant heat transfer. Much can still be learned about radiant heat transfer particularly with regard to the most effective

forms of wall surfaces for furnaces, the reflecting power of various refractories, the radiating effect of gases, and in the case of powdered coal the screening effect of the flame and of the products of combustion on radiant energy waves. A better understanding of these factors will permit still further improvements to be made in furnace designs.

One of the most significant factors in recent stoker and pulverized coal developments is the great increase in efficiency at high ratings. Tests have been reported on the boilers and economizers at the Huntley Station, Buffalo, where the combined efficiency did not fall below 85 per cent at any rating up to 500 per cent. These results are significant of the remarkable progress in combustion methods, furnace design, and disposition of heat absorbing surfaces, that has taken place during the last few years.

### FURNACE WALLS

The quality of refractories for use in furnace walls and arches has been steadily improved both in America and in Europe. Highly refractory clays, silica, alumina, and carborundum have all contributed to this improvement and better methods of blending and burning these materials have resulted in improved refractory brick and tile. With every increase in the temperature that the refractory walls will stand, operators have increased the furnace temperature itself through the use of less excess air, so that these operators next demand a refractory that will stand still higher temperature. While many refractories are available which are serving admirably under given furnace conditions, it is doubtful if one can be produced that will meet all service requirements at the highest temperature that a boiler operator can develop with a low percentage of excess air and a highly preheated air supply.

These limitations of solid refractory walls led to the introduction of hollow refractory walls cooled by the air used for combustion. These have proven satisfactory with some coals when low rates of combustion are the rule. Their use in the upper portion of certain stoker furnaces may produce a cheaper setting than by the use of a complete water-cooled wall. In powdered coal furnaces, air cooling and low rates of combustion lead to large furnace volumes. Where air cooled walls in such furnaces are sprayed with liquid ash, or have flame impinge upon them, erosion of the brick-work is rapid. Some refractory surfaces may be needed with wet, low volatile bituminous

coals to maintain satisfactory ignition and combustion particularly with chain-grate stokers. Air-cooled walls are also desirable for boilers operating at low ratings with powdered coal, for many burners fail to produce adequate turbulence at light loads. Air cooled walls are commonly used in furnaces for small boilers where the expense of a completely water-cooled furnace is not warranted. If sufficient excess air is admitted to control the furnace temperature to that which the refractories will stand, air-cooled walls will prove satisfactory at some sacrifice in efficiency.

Difficulties have been experienced with spalling of refractories. Frequently this is not due to faulty structure of the brick itself, but to the fact that large masses of fused clinker which adhere to the furnace walls, contract in cooling and in the process of shrinkage, portions of the brick to which it is fused are cracked off. This gives the brick the appearance of spalling.

Refractory walls will continue to be used in boiler furnaces with stokers which will not be subjected to high ratings. With powdered coal, the demand for smaller and cheaper furnaces, for higher rates of combustion in the furnace and for lower boiler rooms will probably lead to the construction of entirely water cooled furnaces which will stand higher rates of combustion.

Increased knowledge of chemical phenomena suggests the idea that some refractories may have catalytic effects on the combustion of coal. Little definite information has been developed along this line. Some work has been done to determine the effect of refractories in catalyzing sulphur dioxide,  $\text{SO}_2$ , to sulphur trioxide,  $\text{SO}_3$ . The studies so far undertaken, while establishing the fact that there is a larger percentage of  $\text{SO}_3$  in flue gases than is generally appreciated, have not definitely proven that the formation of this gas is due to the catalytic effect of the refractory walls. Tests at Calumet Station, Chicago, showed that the amount of  $\text{SO}_3$  in the flue gases was greater than  $\text{SO}_2$  with powdered coal burning and both were greater than with stokers on the same coal. It is quite possible that the ash in the coal itself may have a catalytic effect on combustion as has been suggested by leading investigators. Gas engineers have devoted much study to the catalytic effect of water vapor in promoting the rapid combustion of water gas, which is a mixture of carbon monoxide,  $\text{CO}$ , and hydrogen,  $\text{H}_2$ . Here again the data are contradictory although Professor Bone in his recent book on "Flame and Combustion in Gases" throws some doubt on whether water vapor

accelerates the combustion of carbon monoxide. Possibly the satisfactory results achieved with unit mills on powdered coal where all of the moisture dried from the coal is carried into the furnace, may be partly attributable to the catalytic effect of this water vapor in promoting the rapid combustion of the volatile matter and of the carbon monoxide first formed around the coke particles.

Sufficient attention has not always been given to the effect of the composition of the furnace gases on refractory walls. In this connection R. G. Sherman and E. Taylor in their paper "Service Factors Governing the Slagging of Boiler-Furnace Refractories," *Mechanical Engineering*, July, 1927, state: "The most important item in the composition of the furnace gases with relation to slagging is the content of reducing gases,—carbon monoxide and hydrogen. The most generally accepted explanation of the greater slagging of refractories in the presence of these gases is the reduction of the ferric to ferrous iron in ash and in brick, and the consequent formation of ferrous silicates which melt at a lower temperature than ferric silicates."

The authors then show by tests that the greatest slagging of refractories occurs on the walls of actual furnaces where these reducing gases exist during the combustion process. A re-arrangement of air admission to care for the complete combustion of such gases as quickly as they are formed, might lessen to an appreciable extent the slagging troubles of many furnaces. This is substantially the result secured by the various forms of air ventilated side walls at the clinker zone of stokers which have been made of refractories, carborundum and cast iron. Such ventilated sections admit air which passes up along the side walls where it meets the hot furnace gases containing the troublesome reducing gases. The excess air combines with the carbon monoxide and hydrogen adjacent to the furnace walls producing carbon dioxide and water vapor which gases are inert towards the refractories. An adequate air supply may therefore be necessary along refractory walls to protect the brick-work by oxidizing the adjacent reducing gases.

Water-cooled furnace walls of the various types cost more than simple walls of refractories. The engineer again faces an economic problem in the determination of the total costs of operation resulting from the installation of either air-cooled or water-cooled walls. The increased fixed charges but lower maintenance on the water-cooled furnace walls, are offset by the higher temperatures permis-

sible and consequently the higher boiler and furnace efficiencies obtainable. The net annual cost from these walls for a given boiler output must be less than the fixed charges and higher maintenance on the less expensive refractory wall, if water-cooled walls are to be installed. Hours of operation, capacity factors and size of units are elements which must be considered in this connection. It sometimes happens that the installation of water-cooled walls, permits such higher rates of combustion, and increases in boiler output, that the peak-load-carrying capacity of the boiler plant is greatly increased. The cost of the added boilers that would otherwise be necessary to carry this additional load would be saved by such furnace operation. The added cost of the water-cooled walls for such high-output service would generally be fully warranted by the saving in total plant investment in equivalent boiler capacity at normal ratings. This practice of providing large water-cooled furnaces which will generate the heat necessary to operate boilers at high ratings over peak-loads, is increasing in the large central stations of America.

#### SLAG ON BOILER TUBES

The formation of slag on boiler tubes is generally due to the projection by the flame of fine ash particles in a liquid or semi-liquid state against the tubes. These fine particles solidify in contact with the relatively colder tubes and gradually build up slag masses often known as "birds' nests." Slag formation is serious in many cases when boilers with horizontal water tubes are operated at high ratings.

This difficulty is common when the flames, or the tips of the flames where combustion of gases is still active, are permitted to enter the tube banks. The remedy is therefore either to increase the furnace volume or to modify the burning process, so that combustion is completed before the gases reach the tubes. When this is not economically possible, the addition of large water-cooled areas in the form of bare side walls or a boiler tube arrangement known as "slag screens" will do much towards lessening the slagging trouble by absorbing the radiant heat from the liquid slag particles carried by the hot gases and thus causing them to become solid before they touch a tube.

The upper portion of the furnace should therefore be water-cooled to the greatest possible extent. Much can be done by studying the effect of various tube arrangements spaced on wide centers and placed

below the regular tube bank to form the so-called "slag screens." It is probably that such tube arrangements will be provided on all new boilers which will be built to operate at high ratings. These slag screens together with means which will effect thorough mixing of gases and more complete combustion down in the furnace itself, should greatly mitigate troubles from slagging and birds-nesting on the boiler tubes.

### PREHEATED AIR

One of the most significant developments in recent furnace construction has been the increasing use of air, preheated by heat recovered from the escaping flue gases. Preheating of the air required for combustion is not a new device, for it was used over fifty years ago in marine practice. However, it is only within recent years that the advantages resulting from its proper application to stationary boilers has become generally recognized. Preheated air will be more widely used in the future since its favorable effects on the combustion of bituminous coal and on steam boiler efficiency have been definitely demonstrated by tests and by operating records both with powdered coal and with stokers.

Preheated air in stokers rapidly dries the entering coal and causes earlier gasification and ignition. This earlier ignition favors more complete combustion and less loss of carbon in the ash-pit. Increased efficiency results from decreased carbon loss. The greater volume of the preheated air necessitates higher velocities through the grate passages and the fuel bed. This tends to agitate the fuel bed, and the resultant blast effect also leads to more rapid and complete combustion since fresh supplies of oxygen are more rapidly provided to the burning coke. Great care must be taken in the construction of ducts and wind-boxes to prevent leakage of preheated air, as this is particularly objectionable in a fire room.

Preheated air is used in many unit mills to dry the coal for pulverized coal firing. It also accelerates the ignition of the powdered coal in the furnace. Its larger volume requires higher entering velocities and greater turbulence in the furnace which tends to produce more rapid combustion with short, hot flames. The development of such turbulent combustion may lead to smaller furnace volumes or to greater fuel burning capacities with the same furnace volume.

Preheated air is also used as a carrier with powdered coal mills operating on the central system. This hot air dries the coal in the

mill itself and eliminates the cost and use of a separate drier. The system is ventilated beyond the cyclone. The saturated air from the vent may form the primary air supply for the feeders. Any dust nuisance from vents is thus avoided.

The increased furnace temperature resulting from the use of preheated air is effective in increasing boiler efficiency provided the boiler surfaces are properly disposed to take advantage of this gain. Heat transfer by radiant heat increases approximately as the difference of the fourth powers of the furnace temperature and of the boiler tube temperature. Hence increased furnace temperature resulting from the preheat in the air, and from more complete combustion, leads to a large increase in the rate of radiant heat transfer, and to higher boiler efficiency. High degrees of air preheat are now sought and temperatures of 300° to 500°F. are being tried on stokers. With powdered coal, the degree of preheat is limited only by the ability of the preheater to withstand the gas and air temperatures. It is said that air preheated to 800°F. has been used abroad. In this country the temperature of preheated air for powdered coal furnaces seldom exceeds 500° to 600°F.

Many of the present systems of pulverized fuel firing are so designed that it is considered necessary to limit the temperature of primary air for feeders and burners to about 250°F. Hence, in such systems only from 80 to 85 per cent of the total air required by combustion is highly preheated. Better burner design may increase these percentages and lead to improved furnace performance.

#### WATER-COOLED FURNACE WALLS

While the desirability of low ratios of excess air on stokers has long been recognized, the disastrous effects of high furnace temperatures on refractories and on slagging of the ash placed practical limitations on the adoption of such low ratios with uncooled furnaces. The high temperatures developed in powdered coal furnaces where the minimum of excess air is generally used, require a wall that can be cooled. Air cooled hollow walls and water-cooled walls of various constructions serve admirably in stoker and in powdered coal furnaces. Powdered coal furnaces with water-cooled walls, when fully developed, will be capable of withstanding the highest furnace temperatures and of eliminating to a great extent the difficulties with slagging ash.

Some have feared that the cooling effect of water-cooled surfaces

would retard the combustion of the coal on stoker grates and of powdered coal particles in the flame and cause smoke at low ratings. It has been found by close observation confirmed by theory and experiment that the cooling tendency of the water walls does not affect combustion when proper mixing and burning conditions have been provided in each type of furnace. Smoke at low ratings has been generally due to poor air distribution and improper mixing of furnace gases on stokers, and little or no turbulence with powdered coal, rather than to the presence of water-cooled furnace walls. These walls in some cases have reduced furnace maintenance to 50 per cent of the cost with refractories.

Many forms of water-cooled walls are now on the market. These include the following: bare tubes in the furnace in front of refractories, bare tubes recessed in refractories, bare tubes and no refractories, Murray fin-tubes, Bailey blocks with or without refractory facings, Drake "cast-on" iron faced tubes, Foster cast iron blocks with tubes expanded into them, and various forms of other cast-iron blocks bolted to the tubes. Experience with the various types has not been sufficiently extensive to indicate the inherent superiority of any one type of construction. Possibly the various types of coal will require different methods of water-cooled wall construction to secure the highest economy.

The use of water-cooled ash pit floors in place of water screens in powdered coal furnaces is extending. This permits better utilization of the whole furnace volume and is said to result in less slag formation in the ash-pit.

Tube failures have occurred in certain water-cooled furnace walls. These have been invariably due either to impure water, or to lack of proper water circulation and proper provision for removing the steam generated in the tubes. This need of rapid circulation in tubes exposed to radiant heat is apparent when one considers the rates of heat absorption at these surfaces. The average rates of heat transfer to the projected area of tubes exposed to the direct radiant head of the flame generally varies between 40,000 and 70,000 B.t.u. per square foot per hour. Tests have indicated that the rate may under certain conditions reach 120,000 B.t.u. per square foot. It will be apparent that evaporation in such tubes must be exceedingly rapid as compared with the corresponding average boiler surface. The mixtures leaving the top of furnace side-wall tubes consist of 50 to 80 per cent by volume of steam. Hence adequate water supply,

rapid removal of steam, free circulating systems, and absolutely clean tubes are necessary to prevent tubes from being burnt out in service. These factors of construction require further study and development.

All evaporating tube surfaces exposed in the furnaces must be water-cooled at all times. It appears that this condition can best be assured by adequate free circulation of water down from the main boiler drum and ample discharge capacity of the steam pipes from the water wall headers back to the main drum. Inadequacy of proper water circulation has probably led to more trouble with water-cooled walls than all other causes combined.

Another factor of great importance in the successful use of water walls is the prime necessity of pure boiler feed water free from any impurities or gases. Hence evaporators are now widely used to provide make-up water, and every precaution is taken against raw water leakage into the condensate through condenser tube packings or elsewhere. Deaeration of feed water must be effected in the condenser or in a deaerator heater to remove oxygen from the feed water. No scale or oxides will form on the interior surfaces of the tubes with pure oxygen-free boiler feed water and hence high rates of heat transfer are possible.

The high cost of water-cooled furnace walls has often limited their use with small boilers. However, when proper consideration is given to furnace maintenance, to the maximum fuel burning capacity of a given furnace volume and to over-all cost of producing a given number of units of steam, the use of water-cooled furnaces will be warranted on a majority of the larger boilers.

#### FURNACE VOLUMES

There has been a decided increase during recent years in the size of furnaces provided for stokers. These are now about twice the size of those common a few years ago and average about 4 cubic feet of furnace volume per 10 square feet of boiler heating surface. Engineers are not in full agreement in regard to the benefits secured by these larger furnaces. Some claim that efficiencies have been improved with the larger furnaces while others hold that these large furnaces are not necessary. Certain installations have shown that preheated air and extensive water-cooling permit much higher ratings in a given furnace than when ordinary refractory walls are used. However, boiler ratings may be increased when large furnace volumes are provided and slagging of tubes appears to be decreased.

One of the greatest gains in stoker furnace operation results from better mixing of the burning gases. Later furnace designs aim to eliminate stratification in the gases and to provide complete combustion with little excess air. Many recent furnaces for stokers provide for this intimate mixing by adding air above the fire in such a way as to create turbulence in the flame.

Furnace volumes with powdered coal are now subject to critical study. Many furnaces have been built which provide 8 to 10 cubic feet of volume for every 10 square feet of boiler heating surface. However, the uses of low ratios of highly preheated excess air, of water-cooled furnace walls, and of highly turbulent short flames, will undoubtedly lead to smaller furnace volumes for given boiler ratings than in the past.

### STOKER DEVELOPMENT

The use of preheated air and the operation of boilers at high ratings have resulted in many changes in stoker design. Obviously the higher furnace temperature and the hotter air will tend to raise the temperature of the metal parts of the stoker that are in the furnace. Tuyeres and chain grate links have been redesigned to provide greater exposed surfaces for heat transfer to the incoming air by which they must be cooled so that their temperature does not exceed safe limits. Larger air passages must be provided to care for the increased volume of the heated air without increasing the fan power. Also provision has to be made for the increased expansion of the metal parts of stokers at high temperatures. Where high degrees of air preheat are employed, provision must also be made for the permanent growth of cast iron parts, or metals will have to be developed for these parts which have very little permanent growth at the temperatures prevailing in the stoker parts. These special metals will increase the cost of stokers.

All of the various types of stokers that are using preheated air are undergoing development and change to meet these new requirements. In some cases troubles have been due to localized burning of tuyeres caused by slag formation. In others, better air distribution through the fuel bed has been secured by modifications of tuyeres and links. Stoker parts appear to be more subject to burning when it is necessary to drop the load of the boiler while the fuel bed and furnace are still very hot. The use of larger areas of water-cooled side walls with stokers will provide more rapid cooling to stoker parts when

fires are thin or tuyeres become bare and the losses from burnt parts should decrease.

High rates of combustion are now common with both chain grate and underfeed stokers. As much as 60 pounds per square foot of grate surfaces may be burned on chain grate stokers. Underfeed stokers of the largest sizes now burn about 75 pounds per square foot. The greater capacity of underfeed stokers to burn coal is shown by these figures. These increases in fuel-burning capacity have been necessary in order to compete with powdered coal.

Larger wind-boxes and careful air distribution are essential with highly preheated air. Furnaces with chain-grate stokers must serve as mixing chambers where the excess air from the ash pit section is mixed with the reducing gases from the admission end. A recent improvement in furnace design for chain grate stokers is the admission of secondary air through the front arch above the fuel bed when high volatile coal is used. This air tends to mix with the volatile matter first evolved from the coal where normally there is a deficiency of air, and to force the whole mass towards the center of the furnace where complete combustion takes place. Furthermore the cooling effect of this secondary air jet lengthens the life of the arches. When no air is admitted through the front arch, the gases in this section are of a reducing nature which, as noted before, may have a deleterious effect on the brickwork. Additional air oxidizes these gases and renders them chemically inert to the refractories. The admission of this overfire air in some cases increases efficiency and in all cases reduces smoke. The turbulence introduced into the flames causes more rapid combustion which tends to keep the flames below the boiler tubes and thus reduces slagging and "birds-nesting."

Front and rear arches are used with chain grate stokers to secure the proper mixture of the burning gases and to accelerate the ignition of the raw coal. Water backs are generally provided at the bottom of these rear arches.

Chain grate stokers seem most suitable for burning non-coking coals high in ash. High ash is necessary to protect the rear end of the chain grate surface from the intense radiant heat of the fire after the carbon has been largely burned out. This stoker is also used with coals having ash which fuses at a low temperature and which would give trouble if disturbed during the combustion process.

One trouble with chain grate stokers is the loss of siftings through the grates. A new form of chain grate has been developed in Great Britain which appears to have largely overcome this difficulty.

Control of combustion has been developed for both underfeed and chain grate stokers by the provision of various zones to which the air supply can be regulated. A more recent development is the provision of automatic control for these combustion zones and this promises further improvements in boiler efficiency. These devices permit the proper proportioning of air to the fuel to be burned.

Some recent designs of underfeed stokers have air-cooled front walls from which a controlled supply of air is admitted over the fuel bed in order to mix with and burn the volatile matter which is evolved in great quantities in this portion of the fire bed. This will also tend to lessen the wastage of refractories in the front wall.

Many new underfeed stoker furnaces have their walls completely water-cooled so that high furnace temperatures and high rates of combustion are possible in such installations. Others have water-cooled bridge walls and a zone of water-cooled side walls extending several feet above the stokers.

Small underfeed stokers are undergoing progressive development. These are now generally mechanically driven with two-speed gear boxes. The steam-driven ram is used only on the smallest sizes of stokers. The wind-box has been divided in some recent small stokers and dampers provided so that the admission of air to the separate zones of the stoker can be fully controlled.

Long stokers of both chain grate and underfeed type have been provided to allow complete combustion to take place before the ash pit is reached and thus to reduce the carbon loss in the refuse. Clinker grinders are used on all large underfeed stokers and are usually double. Deep ash pits are provided on underfeed stokers where the carbon residue may be more completely burnt out before the clinker grinders are reached. Hydraulic sluicing for ashes is a common practice in large plants. Small stokers will retain the usual ash pit below the stoker from which the ashes are dropped periodically into cars or trucks. The power requirement of stokers are not large ranging from 4 to 10 kilowatt hours per ton of coal burned.

Both types of stokers pick up load slowly from a banked condition and take from twenty minutes to an hour to get into normal service. This may often be a serious matter where loads come suddenly to the station.

Stoker speed for satisfactory operation must be capable of variation over a wide range. Steam engines for stoker drive were superseded by variable speed motors with change gears. Recently a hydraulic

drive has been developed which has a wide speed range with an infinite number of speeds.

In all stokers there is a deficiency of air at the front end and combustibles such as CO and H<sub>2</sub> occur in the furnace gases. Excess air enters through the rear portions of the stoker which are largely covered by ash. The problem is to secure effective mixing and complete combustion of these gases. Violent turbulence and mixing would bring the desired results. Can stoker operation be modified to secure this turbulence so that similar small amounts of excess air may be used as in current practice with pulverized coal?

#### DEVELOPMENTS IN POWDERED COAL FURNACES

Much has been written recently about powdered coal equipment and furnaces so that the subject need be only briefly discussed in this paper. This is no unanimity of opinion as to whether the central system or the unit system of firing produces the lowest total costs. Various unit systems have been applied to large central station boilers to an increasing extent in America. The simplicity of these plants makes them a strong competitor of stokers in the matter of first costs and has forced the makers of central pulverizing plants to simplify their systems and adapt them to smaller space requirements. Some of the new central systems installed in England show marked advances of reductions of space requirements and first cost.

Pulverized coal firing appears to produce in daily operation higher average boiler and furnace efficiencies than with stokers. On the other hand, the cost of power for grinding, transport, and feeding is still a large factor which offsets to an extent the above gain in efficiency.

Powdered coal furnaces do not require any fuel when on bank. They can pick up load again in the course of a few minutes. These furnaces are therefore particularly fitted to plants that must carry sudden demands of load.

Different varieties of coal can be burned in the same furnace with less difficulty than with stokers. This permits more latitude in buying coal for powdered coal plants.

Plants with air-cooled refractory walls generally operate at combustion rates of 12,000 to 15,000 B.t.u. per cubic foot per hour. Exceptionally good test and monthly efficiencies have been obtained on this type of installation. Water-cooled walls permit the combustion rate to be increased to 25,000 or 40,000 B.t.u. per cubic

foot per hour depending on the degree of air preheat, the method of firing and the extent of turbulence in the flame.

The best combustion of pulverized coal occurs when the coal particles are extremely fine, the air supply is highly preheated and the maximum degree of turbulence exists in the furnace after leaving the burner. Fine grinding is expensive so that a compromise on particle size has to be reached that gives the lowest total steam cost. Total power demands usually range from 16 to 28 kilowatt hours per ton of coal burned.

The importance of continued turbulence in the furnace itself as a means of accelerating the combustion of pulverized coal is now becoming generally recognized. Turbulence is necessary to sweep away the products of combustion that surround a coal particle after ignition has started and to provide this particle with fresh supplies of oxygen to continue combustion. The more rapidly this supply of oxygen is furnished, the faster the combustion, the higher the flame temperature and the better the furnace efficiency. Turbulence must not only be set up in the entering mixture but should be maintained in the furnace itself during the entire combustion process. Horizontal turbulent burners should develop such high rates of combustion that the flame will not extend more than 15 feet from the burner outlet. It is significant that the vertical long-flame burner is being discarded in England in favor of the horizontal turbulent burner.

Others have called attention to the danger of too short flames. The carbon particles which remain after the volatile gases are driven off, burn more slowly than the gases. These unburned particles may be projected beyond the short flame and be cooled by radiation before combustion is complete which would result in a high loss of unburned carbon in the flue gases. This, however, in no way lessens the importance of violent turbulence in the furnace.

Turbulent burners are a recent development and many improvements can be made on them to lessen the possibilities of burning out the metal parts, to improve operation at low ratings, to speed up ignition after leaving the burner, and to ensure more rapid combustion in the furnace.

Most of the turbulent burners are of the horizontal type. This form is generally used with unit mills. Several forms of tangential firing produce great turbulence by their cyclone effect and have developed high rates of combustion. This method of firing will also be used more extensively.

Bituminous coals, low in volatile matter, take a longer time to burn than those high in volatile constituents. Hence the carbon loss up the stack will be greater with the low volatile coals when the same furnace volume and flame lengths are used. Coarse grinding also leads to slower combustion and higher carbon loss up the stack. Greater attention should be directed to these carbon losses and to means whereby these losses could be diminished.

The trend of development in powdered coal furnaces is towards the employment of water-cooled walls on all sides, particularly when high rates of combustion will be employed. Considerable refractory surface is used in many furnace designs. It seems probable that refractory areas will be decreased and more bare-metal wall surfaces will be exposed directly to the flame in future designs particularly when violent turbulence is employed. In some cases steam-cooled side walls in the form of radiant superheaters have been used in place of tubes with water circulation.

One of the most troublesome features of powdered coal furnaces is the ash in the coal. The liquid ash particles in the flame are dashed on to the water-cooled wall surfaces. The rapid cooling of the ash on the metal causes it to crack on sudden cooling, to adhere only loosely, and to drop off into the ash-pit from time to time. This ash is generally removed from the furnace bottom and carried away by some form of water sluice. Some furnaces are now in operation where a refractory hearth has been laid on the furnace bottom and the ash which drops down is maintained in a liquid condition by the radiant heat of the furnace and tapped out from time to time. It is disintegrated by a water jet as it leaves the furnace bottom and breaks up into a fine sand-like substance. This type of furnace would seem best suited to coals with an ash of low fusing temperature.

The greater part of the ash is carried away as a fine dust in the chimney gases. Many schemes have been tried to catch this dust such as cyclones, dust-catchers, washers, and Cottrell precipitators. The use of water sprays is under development and promises to remove a greater part of this dust in a cheap and simple manner. Tests of spray washers at Calumet Station, Chicago, indicated that 90 per cent or more of the dust was removed. The dust that finally escapes from the chimney may be deposited in the immediate neighborhood or may be transported over considerable distances depending upon climatic conditions. Fair winds and a dry atmosphere favor transportation for a long distance; still foggy air causes the ash to

settle around the plant itself. In any case ash is a nuisance and engineers should make special efforts to reduce the amount leaving chimneys. Another problem before engineers is to find some economic use for the fine ash from powdered coal furnaces.

### AUTOMATIC COMBUSTION CONTROL

An outstanding advance in the operation of boiler furnaces has resulted from the development and application of automatic combustion control equipment. Quite a number of different systems have been tried for this purpose; among these are the Bailey, Smoot, Hagan, Engineer Company, Carrick, Gibson, and Hess. All of these have been installed in one or more large electric central stations and are said to have given satisfaction. Automatic combustion control is a new art and many intricate problems had to be solved before the equipment operated properly. Many ingenious devices have been developed to meet the contingencies of plant operation. While some of these systems have been in use longer than others and have thus been more highly developed, all may be considered as in their early stages of evolution. It is probable that many modifications will be made in each system to improve its operation, to simplify the mechanism, and to build it so that supervision, checking, and adjustment will be less than at present. For instance, in some systems it is present practice to use hand control in building up or removing the load from boilers. Sudden great demands for steam may also require hand control for a short interval. Few automatic controls are operating 100 per cent of the time.

These various automatic systems take the control of combustion largely from the fireman and transfer it to the machine. The personal element is replaced by mechanical devices actuated by some factor of the boiler operation such as steam pressure, steam flow or air flow, by means of which the operation of the boiler can be made to approach some set standard.

Experience in central stations indicates that a more constant steam pressure can be maintained at all ratings by automatic than by hand control. Lower quantities of excess air are admitted since the controls endeavor to change air and fuel quantities in their proper proportions. These conditions improve the fuel bed with stokers, and higher furnace temperatures are developed. Loads can be divided more equally between all boilers by automatic control, and fluctuating loads are easily handled. These controls save

considerable labor on the part of the operator. Finally, it is the general opinion that automatic control produces higher continuous boiler efficiency than hand control. Gains of several per cent are claimed in some cases and this alone would warrant the extra cost of this additional machinery.

These advantages appear to justify the installation of automatic combustion control both with stoker and with pulverized coal furnaces under large boilers. An extending use of such equipment may be expected in the future.

#### TREND OF FURNACE DEVELOPMENT

The preceding paragraphs have indicated certain trends in the development of boiler furnaces for burning bituminous coal both on stokers and as powdered coal. In general furnaces will be built to secure maximum heat generation per cubic foot of furnace volume with minimum excess air quantities and hence high  $\text{CO}_2$ . As a consequence, the highest possible furnace temperatures will be developed, and this will lead to increased heat transfer and improved efficiency. All furnace walls will be water-cooled to permit these desired operating conditions at high ratings, and this construction may be expected to become standard practice.

Ash difficulties may be lessened by better raw coal preparation at the mines so that less ash is received at the plant.

The development in powdered coal equipment forced stoker manufacturers to make such improvements in stoker and furnace construction that the competition between the two forms of firing is now intense. As a consequence of this, one may expect further improvements in both methods which will lead to better efficiency and to refinement of equipment. Turbulence permits complete combustion and maximum furnace temperature with minimum excess air for powdered coal. Overfront air admission and arches tend to mix furnace gases on stokers. Future development will provide still greater turbulence in stoker furnaces as well as in those for pulverized coal.

The end of improvement in equipment for burning bituminous coal is not yet in sight and one may look forward to the development in the near future of still better, simpler, and cheaper furnaces.

# THE KILOWATT HOUR AND THERMAL ECONOMY OF ITS PRODUCTION

By A. R. SMITH

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The kilowatt hour has now become one of the major products of the United States and considering its youth and the uniform and rapid increase in consumption it promises to exceed in value the yearly production of many other products which have heretofore been used as indexes of business conditions. Some conception of the relation of the yearly kilowatt hour output to other common products, expressed in millions of dollars a year, can be gained by reference to the accompanying curve.

The kilowatt hour, being a unit of energy, has unlimited application and while some of the present applications may have reached saturation, its field of utilization is being constantly extended to such a degree as to assure a steady and material increase in consumption for many years to come. In fact we can have no accurate conception of the size of this infant industry thirty years hence, because we do not know how intensive and general illumination will become; how much electric heat may encroach on other methods of heating on account of its desirable characteristics; and how extensive a part electrical power is going to play in the field, in the factory and in the home as civilization progresses.

We do know that the yearly consumption is approaching a hundred billion kilowatt hours and that it may reach two hundred billion early in the 40's, if the present rate of increase continues. This means that during the next 12 or 15 years power plants must be built having an aggregate capacity equal to all that are now in existence, in addition to the demand for new plants necessary to replace existing ones, which may become obsolete, inadequate or worn out, although some of the latter may be provided for by still greater interconnection and coördination. The demand is not a question of the shortage or over production or any particular crop of any particular product, but rather is associated with the prosperity of the country as a whole which is reasonably sure of a good average over such a period.

For the past several years, one-third of the electric power consumed in the United States has been produced by hydraulic power and two-thirds has been produced by steam power. This ratio

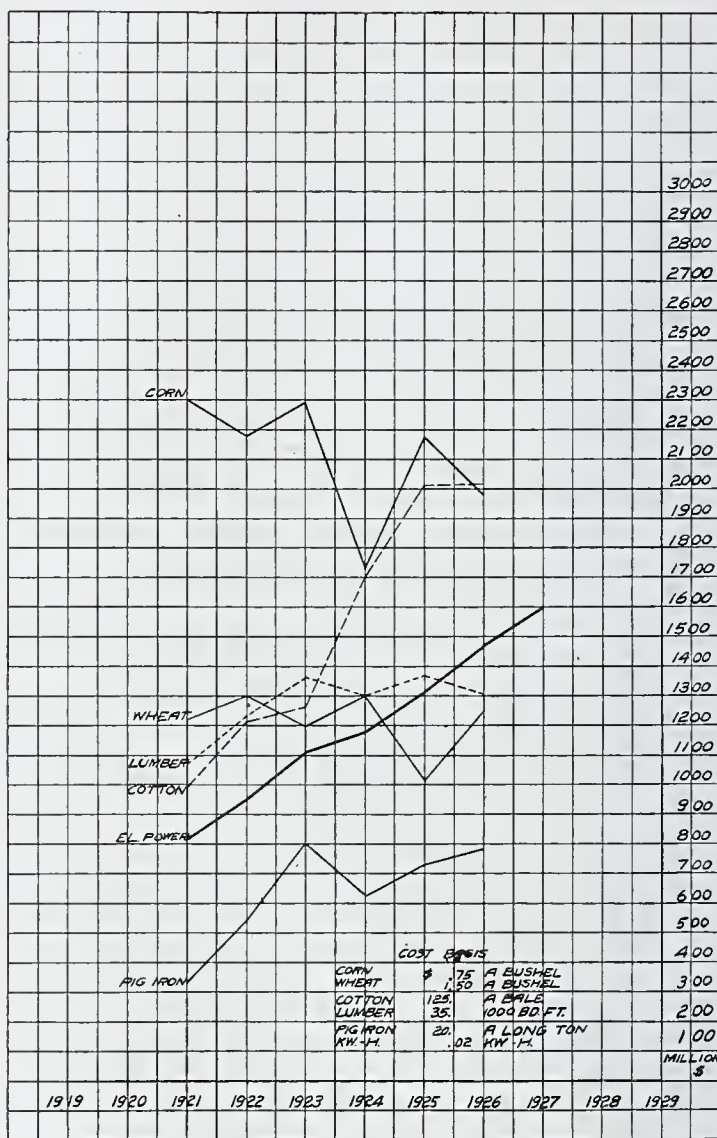


FIG. 1

has held so constant that there is little likelihood of a material change during the next 15 years. As the available water power sites are considered, the more expensive developments are generally

postponed which is one reason to expect that the unit cost per kilowatt of capacity will have a tendency to increase. On the other hand, the modern steam electric power plant, a keen competitor to most hydro-electric stations insofar as the total cost of delivered power is concerned, can probably profit far more by advancement in science both as to initial cost and fuel consumption. Further improvements in the steam plant may, therefore, put the hydro-plant on the defensive and alter the prevailing ratio to a far greater extent than would be expected.

The hydro-electric plant, however, is going to remain an important factor in electric power production. The more expensive developments may be delayed because of advances made by the steam plant but they will ultimately be developed. The hydro-electric plant has some indisputable qualifications which are assets to the owner and to the nation. The major portion of the investment is in structures, which if properly constructed, should last down through the ages. Most of the machinery is operated at low speed, low pressure and low temperature and has an exceedingly long life. The efficiency of converting potential water power into electrical power is so high that new apparatus cannot usually be justified at a later date on the strength of improved efficiency or increased output. A good hydraulic plant is a legacy to posterity and should have a low depreciation rate as compared with a steam electric plant.

Of the total power not generated in hydro-electric plants 90 per cent was produced during the past few years from coal and 10 per cent from oil and natural gas, the bulk of the two latter fuels being used to make steam for power with a small percentage consumed in internal combustion engines. This leaves 60 per cent of the total power consumed to be made from coal with only a negligible percentage to be made from anthracite coal.

The conversion of heat energy into mechanical energy and electrical energy is quite difficult and relatively inefficient. In other words, there is much latitude for the scientist and the engineer to introduce more efficient heat cycles, more suitable equipment and especially better temperature and heat resisting metals.

There is also a great opportunity for a good commercial method of decomposing bituminous coal so that its more valuable constituents can be salvaged for a general market and the residue consumed for the production of electric power on a vast scale.

The medium used to limit the temperatures of the metal in boilers

and turbines and elsewhere is steam and the steam cycle has proven very satisfactory and has been highly developed. In the endeavor to get higher thermal efficiencies, the steam pressure has been raised to a point where there is little more energy available and the superheat has been raised to a point where special metals will have to be employed to permit any further increase in combination with the higher pressure.

The theoretical heat energy available with 1,200 pounds, 700°F. initial conditions and 1"Hg absolute final condition in a regenerative, reheat cycle, is approximately 47 per cent which with 85 per cent boiler and furnace efficiency and allowing for the turbine and generator losses and station auxiliary power brings the overall efficiency down to about 31 per cent and this, at full load ideal condition. Prevailing operating conditions with commercial loads may lower this to about 29 per cent. Records of performance on a 600-pound steam cycle have already been recorded at 27 per cent and it is, therefore, expected that some of the existing or projected 1,200-pound plants will shortly show 29 per cent or possibly better.

Figure 2 is plotted to indicate the possible trend with respect to time and to show the relation between available heat, net available power, best station performance and average station performance. The average efficiency of all steam plants in the United States as best can be determined from general statistics for 1927 was 14 per cent, but this has been steadily improving since 1919 when it was only 8 per cent. This rapid increase is probably due in a large measure to the increase in the percentage of power produced by the large high efficient steam plants.

With still further increases in steam pressure and superheat and refinements in the regenerative, reheat cycle the heat available might be raised to some 50 per cent, which with further improvements in apparatus efficiencies it might be possible to reach an operating efficiency of some 34 per cent. But to do this may mean increasing the investment so that the excess fixed charges equal or exceed the gain made in fuel economy.

The other cycle applicable to production of power in large volume and which has been proven on a commercial scale is the binary vapor cycle, which superimposes a mercury vapor cycle over the ordinary steam cycle. This gives some 60 per cent as against 47 per cent theoretical energy available previously referred to and has some promise of a still further increase in efficiency by raising the mercury vapor pressure if suitable high temperature metals are employed.

With the relatively high overall thermal efficiency of 30 per cent the cost of fuel per kilowatt hour would be 0.22 cents with coal having a calorific value of 13,000 B.t.u. and costing \$5 per net ton. While this amounts to shrinking the fuel cost pretty nearly 50 per cent compared with the best stations of ten years ago, it still represents in the aggregate a yearly expenditure worthy of the most intensive study and experimentation to still further reduce it.

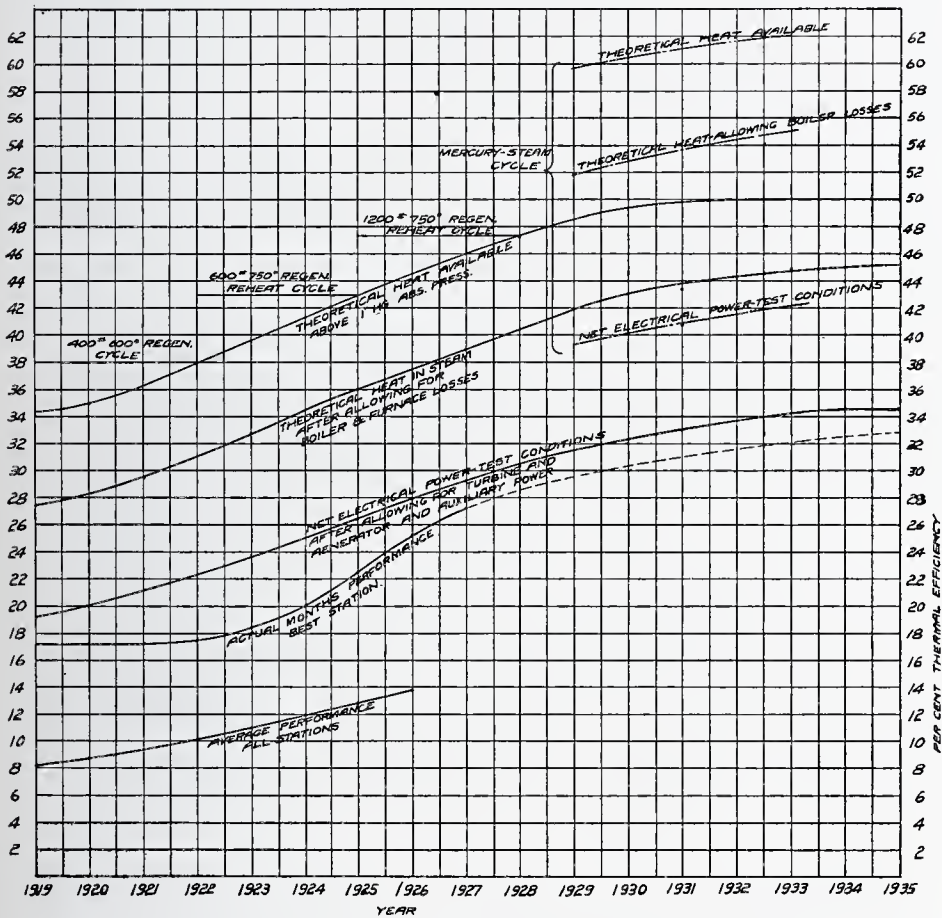


FIG. 2

With no immediate promise of materially improving the steam cycle, it is logical to seek other steaming fluids or combinations. Water is abundant and in years gone by when the make-up required was 10 or 20 per cent it was essential to use a cheap steaming fluid. With the low percentage of make-up now required by a modern steam plant and with the high degree of purity demanded for high

steam pressures, it becomes a question if we should not use a fluid which may cost more initially but which would not be so liable to contamination.

It is pretty well known now that with extra high pressure steam the water must be kept in suitable condition as regards air content, acid content and alkali content. While there must be some salt in the water to assure a non-acid condition, this salt must be such that it does not vaporize at the steaming temperature, and does not tend to cause caustic embrittlement of the steel. To maintain water at such a perfect state required constant vigilance because so many materials are soluble in water.

Mercury, considered as one alternative steaming fluid, entails a higher investment, but it is an ideal steaming fluid for dealing with the higher temperatures and it is easily maintained in a sufficiently pure state to serve the purpose of making vapor. It is true that in the mercury vapor cycle the steam cycle must be used at the low temperature end, but the steam is made with a temperature differential of only 15° or 20°F. between the mercury vapor and the steam. Therefore, there is no danger from tube failure due to scale formation and there appears to be little or no scale deposit because of this slight temperature differential. At all events, it appears that almost any character of water can be used for the steam cycle of the mercury-steam combination and that deaerators, evaporators and special treatment or constant testing are not essential. This leaves the steam cycle relatively inexpensive and simple to operate.

Whatever may be accomplished along the lines of improving the heat cycle should not prevent our attempting to introduce new combustion cycles which may lower the cost of fuel chargeable to the power plant or lower the investment of the power plant, because new combustion cycles may be the means of introducing new heat cycles.

By "combustion cycle" I mean the cycle whereby fuel and oxygen are put together for the purpose of producing heat. The idea of returning some of the heat from the products of combustion by preheating the air is in a sense a different cycle than when no preheat is used. The use of heat from the products of combustion to heat the fuel, the idea of first gasifying the coal and then burning the gas, and two stage combustion are other cycles. In the past we have not viewed combustion in just this light, but I think that in the future we will specify what method or what cycle of combustion is proposed.

I prefer to use the term "combustion cycle" in order to differentiate it from the heat cycle which, as commonly used among engineers, refers to the conversion of heat into power, whereas the combustion cycle refers to the production of heat.

If we could successfully segregate coal into its component parts at a high thermal efficiency and with a reasonable investment, it may present opportunities to lower the cost of fuel chargeable to power and possibly lower the investment cost of the power plant. There are two interesting methods; first, to produce as by-products domestic coke, tar oils and gas and to burn the coke breeze or any of the residue fuel for making power. This method may materially reduce the cost of fuel for power, but it will not lower the investment cost of the power plant. Perhaps the most serious objection to it is that several times as much coal must be carbonized as would otherwise be needed for producing power, which tends to make the power plant secondary to the coal carbonizing plant.

The second method, which has considerable promise, is to gasify the coal completely, extracting the tar oils or the light oils for sale and using the gas for the generation of power. Such a method would not reduce the cost of fuel chargeable to power as much as the first mentioned method, but it would open up innumerable opportunities of reducing the boiler room investment.

Some studies that have been made of a combination steam power plant and gas plant have failed to make a good showing because of the low thermal efficiency of the gas plant. To offset the low thermal efficiency, a high evaluation of the by-products has been used, but the market is not sufficiently stable to assure high prices for any long period of time. Steam production efficiency using gas is no better and may not be as high as steam made from coal on account of the greater hydrogen content of the former. Consequently as little steam should be used as possible in the gasifying process. If steam is produced at 85 per cent efficiency and gas at 80 per cent, the overall thermal efficiency is but 68 per cent, which is low compared with the up-to-date coal fired boiler. But, if gas can be produced at 90 per cent thermal efficiency, there is some hope of a combination plant competing with a coal burning plant.

Sufficient attention has not been given to the possibilities of more complete coördination of gas making and power production. The tendency has been to determine the cost of different grades of gas and then to estimate the power cost when using such gas as fuel.

What is wanted is essentially two stage combustion, in the first stage of which the tar oils are salvaged and the ash removed, all of which can be and should be accomplished at low temperature. The second state should be operated at high temperature for the production of steam at the highest efficiency with compact and simple equipment having little thermal storage.

The ash in the coal, especially if the coal is burned in pulverized form, is a very troublesome factor. Formerly, it was removed as dust which necessitated keeping a portion of the furnace temperature sufficiently low to prevent slagging, now there is a tendency to remove the ash as a liquid which demands a higher temperature in that part of the furnace where the ash is deposited.

But only a portion of the ash content (10 to 40 per cent) is deposited in the furnace, the remainder passes on through the boiler and out the stack or remains on the heating surface as slag. To catch the fly ash before it reaches the stack is not only difficult and expensive, but it is a problem to know what to do with it after it is collected. The slagging of the heating surface, if allowed to persist, may put the boiler out of commission in a few hours, due to stoppage of the gas passages.

If a dustless, ashless gas, regardless of calorific value, were available, the boiler design might be altered materially; the combustion temperature might be increased; the size of the combustion chamber reduced; more radiant heat absorbing surface might be introduced and the gas passages changed to advantage. In brief there is much latitude for the boiler designer to produce a high pressure steam or mercury boiler of high efficiency and low initial investment.

To neglect to heat the feed water to the maximum temperature practicable by the extraction of steam from a turbine is overlooking an opportunity of improving the plant economy. Furthermore, the logical arrangement is to make the turbine room cycle complete in itself and to deliver the feed water to the boiler plant at as near steaming temperature as is practicable. On the other hand, the boiler room should heat the combustion air to as high a temperature as possible, thereby making the combustion cycle regenerative.

Regeneration on the combustion cycle has not been carried to the possible limits; first, because the stokers could not use extremely hot air and second, the pulverizer, if using the same air for pulverization and combustion, would not perform properly due to the plasticity of the coal. Aside from the fuel burning and preparation equipment,

the furnace temperature became too high and tended to cause slagging of the ash or over heating of the boiler tubes.

If a clean gas is used as a fuel, if the furnace is completely water jacketed and if the boiler circulation is made more perfect, the furnace temperature can be raised very materially. With the tendency of a higher furnace temperature, more heat can be transmitted in radiant form and more radiant heat absorbing surface can be installed to replace convection heating surface. This might be accomplished by dividing the combustion chamber into smaller units, thereby getting more surface per cubic foot of combustion space. The whole idea would be to raise the average temperature difference between the steam generating surface and the furnace and to remove the low grade heat by returning it into the combustion air which is an all low pressure process.

To put more heat in the combustion air entails larger air preheaters, which have a limited life and being made of metal must be kept within the usual temperature limitations. It is possible, however, to substitute the recuperative preheater using gravel or refractory or cast iron and carry the combustion air temperature up to 1,000°F. Such apparatus would be bulky and heavy but crude and could be located out of doors similarly to blast furnace stoves. Such preheaters naturally would have large thermal storage, but thermal storage, external to the boiler and controllable as this would be, is very desirable.

If the combustion air could be preheated to 1,000°F. and the products of combustion left the boiler at 1,200°F., the high pressure steam boiler would be working at a much higher mean temperature differential than at present. Most of the heat could be removed in radiant form; there would be little thermal storage in the boiler uncontrolled and an abundance of thermal storage external to the boiler under perfect control.

Raising the temperature of the heat cycle means raising the temperature of the combustion cycle. Water cooled furnaces remove one objection to high combustion temperatures; the use of gas as a fuel would remove the other objection, namely, the slagging of the ash. However, the new scheme of drawing off the ash as liquid may be found suitable for such high furnace temperatures providing suitable provision is made to prevent the slagging of the heating surface.

Such a high temperature combustion cycle might be particularly

well adapted to the mercury cycle. The mercury boiler proper could reduce the temperature to 1,200°F. and the steam superheater might be used to protect some of the furnace walls and the outfit would be simple and not unlike the usual steam boiler.

Gas fired boilers could be located out of doors in almost any climate as they should require little attention and few repairs, and could be automatically controlled to perfection. With recuperative air preheaters of large capacity, the boiler could be made in single large units, or could be subdivided into as many units as found desirable, as the investment would not be greatly increased thereby.

If a steam electric plant has a first cost of \$100 per kilowatt of capacity and operates on a 50 per cent capacity factor, the fixed charges, if taken at 15 per cent, amount to 0.343 cents; this, it will be observed, is a greater factor than the fuel cost per kilowatt hour. A good share of the investment cost is boiler room building and coal and ash handling equipment. The latter would become a part of the coal gasifying plant and the former could be largely dispensed with. The boiler and furnace should be considerably cheaper and on the whole there would probably be more than enough capital saved in the steam plant to pay for the gas plant.

We prepared some time ago a study of a combination gas and steam plant based on complete gasification of coal in large single retorts to be operated at moderate temperatures and using a small amount of steam in the process, for the purpose of getting some conception of the possibilities of reducing electric power production costs. The results are shown on the curves in Figure 3 which are based on 90 per cent producer efficiency, 20 gallons of tar oil yield per short ton of coal at a value of 5 and 6 cents per gallon and with coal at varying prices.

The estimates included fixed charges on the capital invested, operation and maintenance costs as well as the fuel cost and the results as will be observed show a balance with \$4 coal and 6 cents oil, with an increasing profit for the combination gas and steam plant, as the cost of coal becomes less. This is to be expected because one of the principal gains is the higher commercial value of the oil when extracted than when allowed to remain in the coal and used as fuel. Consequently, the greater the differential between the cost of coal and the price of oil, the greater will be the profit.

Figure 4 illustrates the type of plant figured on. The gas generating equipment and the boilers are all located out-of-doors while the

latter are supposed to be fired by surface combustion methods to reduce the furnace volume. All equipment would be automatically controlled as far as practicable from a central control room overlook-

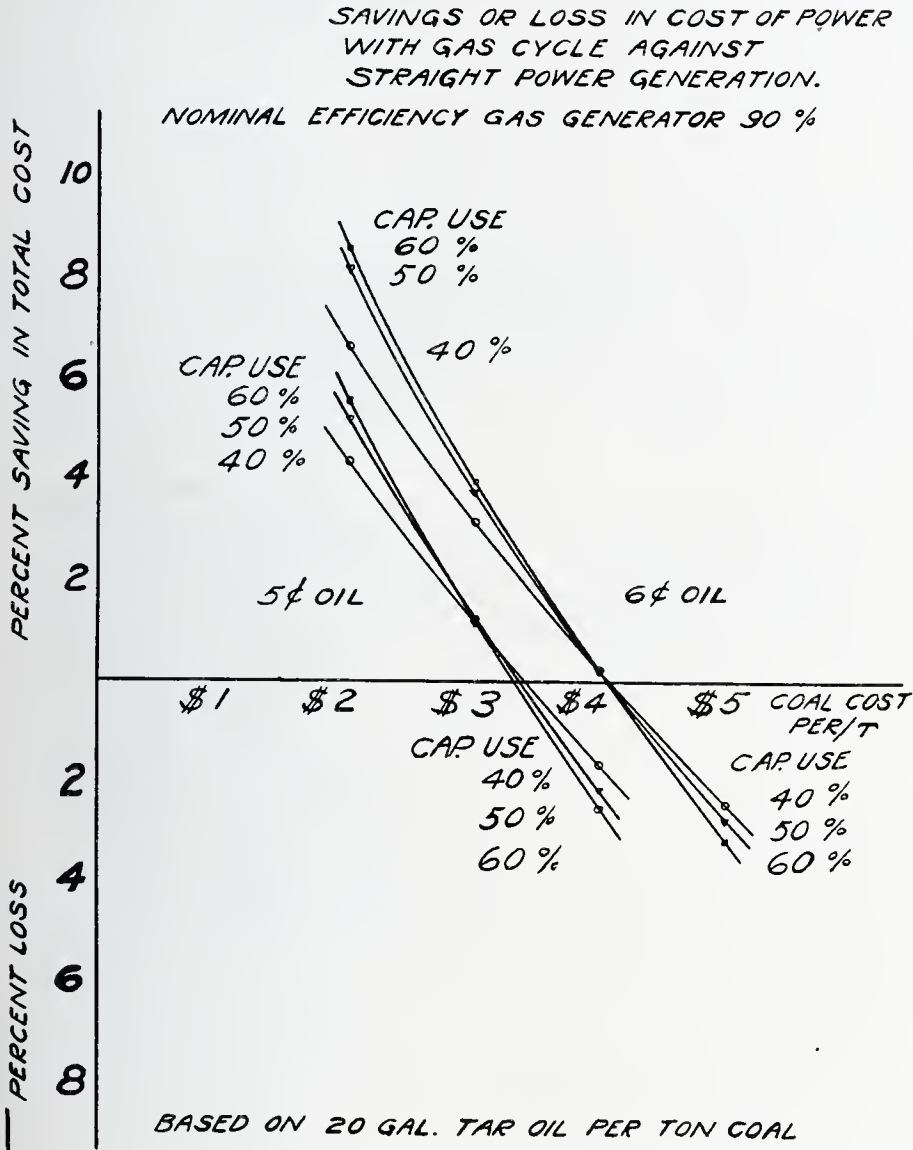


FIG. 3

ing the turbines, boilers and gas generating equipment. Many refinements might be added which would contribute to improve the efficiency or reduce the investment such as the use of larger boiler

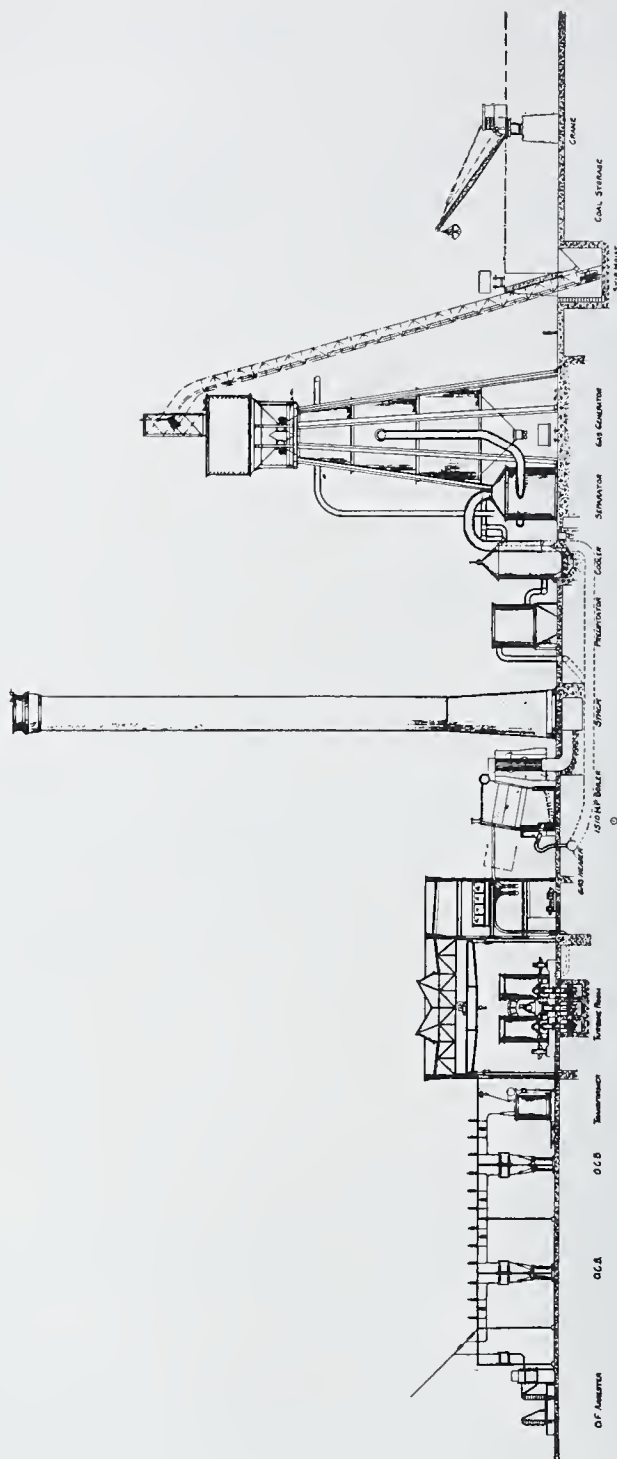


FIG. 4. ELEVATION OF GAS-ELECTRIC POWER STATION

units; the extraction of steam from the turbine to enrich the gas and the reduction of the percentage of gas carrying the tar oil so as to reduce the heat loss in the condensers and scrubbers.

In conclusion the author would like to suggest that this study and others which have been made previously indicate sufficient possibility of gain from a combination plant to warrant others studying this same problem along somewhat different lines of attack.

### DISCUSSION

H. L. RICHARDSON (West Kentucky Coal Company, Paducah, Ky.): Has Mr. Langtry any records concerning the fusion point of ash of coal mixtures? I have had some difficulty with mixtures of two seams of coal in my district, and the fusion point of the ash of the two seams was quite different. I invariably find complaints from customers who receive a mixture of coal from the two seams. I have had no analyses made of the mixture. I wondered if Mr. Langtry could inform me as to the action of the mixing on the fusing temperature of its ash as compared with the fusion points of the ash of the individual seams.

MR. LANGTRY: I am glad to say we have done some work along that line. That is the feature I mentioned in this paper in the last paragraph. We are continuing this investigation and through this next year we intend to take different coals where we are positive of their origin, and mix them on a different percentage basis. Results we have had so far have shown that the fusion temperatures in some cases will fall in between the two individual fusion temperatures. In some cases it will rise, in others, it will fall. There seems to be no set rule from the investigation we have carried on so far.

Mr. Kohout, who is a joint author of this paper, might have something to say from the chemical standpoint.

MR. KOHOUT: As far as the work has progressed, there has not been enough data collected to form any positive conclusion. Very often the fusion point of the mixture will be almost the average of the two. In some cases, as Mr. Langtry mentioned, it will drop below the fusion point of either one.

The chemical analyses of the ashes have not all been made yet, so we can not tell just exactly what parts of the constituents are really to blame due to varying composition of the ash itself. So far we can only report on a few of the fusing points themselves, and they will vary from below the fusing point of either of the constituents of the mixture to above either constituent. Just why, we have not carried the investigation far enough to find out.

O. O. MALLEIS (The Koppers Company, Pittsburgh, Pa.): We have made a number of mixtures of coals of different fusion points, and I believe in nearly all our cases the fusion point of the mixture was between the fusion point of the two individual coals. Usually, I believe, it was less than the average. I think that this is the tendency in general but it may, of course, vary with different coals.

MR. LANGTRY: Do you remember what your percentages were?

MR. MALLEIS: We varied from 90-10 down to as low as 50-50. In nearly all cases I believe the fusion point of the mixture was somewhere between the fusion point of the individual coals. When only 10 per cent was added I think it was nearer the fusion point of the lower coal.

CHAIRMAN HUNTER: The subject of "fusion points of ash" is one of the most important things in the burning of coal. Are there any further questions?

WILLIAM C. SKINNER (Fuel Saving Heater Corporation, Cleveland, Ohio): I am sincerely interested in the question of burning soft coal by a process which will eliminate smoke and clinkers in residential furnaces. I am therefore very much pleased with all that has been presented to us in the paper under discussion.

In Mr. Langtry's experience, I would like to ask, if the burning of waste paper in residential furnaces is as detrimental from the standpoint of fuel economy and effecting the "fusing point" as is the case in the burning of garbage? Or in his judgment, in the burning of waste paper on the top of the fuel bed in any residential furnace, would the fusing point of the fuel be effected and a clinker state produced, same as in the burning of garbage?

The burning of waste paper and the burning of garbage in residential furnaces seems to be a common practice in Cleveland. In my experience with householders, the installation and service pertaining to their furnaces,—a definite loss is sustained and the efficiency of the furnace greatly reduced in the burning of waste paper as stated.

I take it for granted this is an educational meeting for those in attendance, no doubt therefore, all here desire to do better work, correct errors and thus bring about better results in this particular line of fuel consumption.

MR. LANGTRY: We have ourselves run no tests at all on paper. If there is a great deal of paper put in and the combustion does not take place too rapidly the paper might have a tendency to seal up inside of the fuel bed some of the intense heat being generated there. That in itself might cause the clinkering of the coal ash.

R. V. KLEINSCHMIDT (Arthur D. Little, Inc., Cambridge, Mass.): I would like to suggest that if the ash from two sources had approximately the same chemical constituents this proportional law would hold in the case of the fusion points. However, if one of the ashes has a different chemical composition, theoretical considerations indicate that there would be a distinct lowering of temperature, particularly if one of the constituents contained potash or soda. In the case of waste paper, there are frequently papers loaded with China clay, and that mixed with the usual types of ash, high in silica and lime, would tend to create a marked lowering in the fusion temperature. This is merely generalization, but I think perhaps it will help to show the general trend.

A qualitative analysis to determine the elements present would give us a

very good indication as to whether there would be a lowering of the fusion point or not.

MR. KOHOUT: So far as paper is concerned, there would have to be a very large quantity burned, because the ash in the paper is quite small. If there were papers being fired pretty steadily for several hours, causing an accumulation of ash, there is no question but that the fusion point in the mixture in the fire box would be lowered so that clinkers would be formed.

As for mixtures of coal or ashes of different compositions, this is what was brought out in the paper. These ashes naturally are greatly different in composition. The first ash that had the high fusion point, No. 61918, was an ash consisting primarily of bone ash, which acted as a flux on almost any mineral ash with which it came in contact. That was why it exerted a much greater effect on the coal ashes with which it was mixed than the other garbage ash. It was purely a fluxing action.

L. A. PIERSON (Frederick Stearns & Company, Detroit, Mich.): With reference to burning vegetable matter of any kind with coal in the furnace, I wish to say that for nearly two years I had experience with this practice and I found that the introduction of any kind of vegetable matter in any very great proportion into the furnace, had a decided tendency to lower the fusing point of the ash. It finally became so bad in our case—and we were only burning about 10 per cent of vegetable matter—that it was necessary to discontinue the practice entirely. It not only made it extremely difficult to keep the refractories clean and to clean the fires, but also had a tendency to mat over the tubes in the boiler furnaces in such a way as to retard the draft, and consequently the rate of combustion.

CHAIRMAN HUNTER: If there is no further discussion, we will pass to the next paper, "Coke Burning Domestic Boiler" by Dr. Charles Brabbée.

H. C. PORTER (Philadelphia, Pa.): I would be interested in knowing whether these tests on the boiler described were run at a constant load, or at such possible variations in load as would occur in house heating under quick changes of weather conditions.

The clinkering of fuel comes when a sudden change of load is put on the furnace to drive it harder. Coke, of course, is a good fuel, if carefully prepared with a view to the purpose for which it is intended. If it is not well prepared as to choice of suitable coals in respect to their fusion point of ash, which would generally mean low ash, low sulphur coals of high cost, then we are likely to run into difficulties in clinkering. I have found many householders complaining of the clinkering of their fires with coke.

Dr. Brabbée stated that the special boiler shown was well adapted to anthracite coal as well as to coke. He gave, as I understood, a comparison of the attendance required as in the ratio of 40 hours with anthracite, to 24 hours with coke, meaning, I take it, that attendance to fill the reservoirs would be required with anthracite only in 40 hours, with coke in 24 hours. We know

that anthracite has a very much larger weight per cubic foot than coke. That is one of the big advantages of anthracite oven coke in firing household heaters. The weight per cubic foot of anthracite may run 50 to 60 pounds per cubic foot, whereas in coke it runs 26 to 28. There is a ratio of more than 2 to 1, a bigger ratio than the 40 to 24, as mentioned in the paper for hours of attendance.

I take it that may come from the composition of the anthracite used, that it may have been a high ash anthracite. His coke ran about 8 per cent. The anthracite used was probably higher considerably in ash. It may be of interest to note that anthracite is available on the market now even in buckwheat form, running as low as 11 or 12 per cent in ash, much of the anthracite being prepared now by new and improved cleaning processes, so as to carry only from 9 to 12 per cent ash in the various sizes. Such grades of coal would bring up that attendance ratio so as to show even a greater difference.

If the anthracite people continue to improve their preparation practice so as to put out very generally a low ash coal, adapted to these magazine-feed boilers such as are being developed so well by the American Radiator Company and others, they will be able, I think, to hold the advantage that comes inherently in their fuel over coke, due to its higher density.

DR. BRABBÉE: In answering the first question, I would like to have my boy here who is attending to the boiler. Since firing the boiler in the house with coke he has not had any clinking at all up to now and he would rather take care of ten of those boilers with coke than one of the old type. Going to school in the morning, he has generally nothing to do with the boiler at all. If the temperature, however, runs lower than freezing point he will add a few shovels in the morning. At night, it only takes him ten minutes and he has had no trouble yet, although we have had pretty sharp temperature changes in the last few weeks.

In the laboratory tests we have found some clinking on high boiler loads. The clinkers are easily broken up and taken out by the special large door. We have here in this house an exhibit of such a boiler installed, and anyone who will go down there can watch what will occur.

Regarding the difference between the fire periods of anthracite and coke, we have used for all those tests coke available around New York, for instance, of the Consolidated Gas Company or Koppers Coke Company, which coke runs between 6 to 7 per cent ashes, which is very little. One of the officials of the coke company has such a boiler installed in his house and he said, "I am a very busy fellow, cleaning out my ash pit only once a week, whereas before I had about 4 barrels of ashes a week. The men taking the ashes away are very much surprised they only find half a barrel a week."

We could not be quite sure of those low ash contents with anthracite. We have asked coal dealers to send us good anthracite for tests and in analyzing we have found much higher ash contents, and that is the reason why the firing periods with anthracite are not very much longer than given.

We all are at the mercy of the coal dealers, because we cannot check up on the heat value and the ash content of the fuel offered, and we can only hope that all fuels will be better gradually with high heat value and less ashes.

P. NICHOLLS (United States Bureau of Mines, Pittsburgh, Pa.): As Mr. Porter said, coke as a desirable fuel for anthracite is granted by all, and as far as its use can be encouraged, and the present objections that users find to it overcome, it will be for the benefit of our atmospheric conditions where we otherwise burn bituminous coal. Other things being equal, a magazine type of feed for coke should give you less trouble in boilers than where the feed is intermittent.

A large part of the clinkering trouble is due to the spasmodic way in which many householders operate their furnaces. The usual procedure is: sometime in the evening the lady will object and say the house is very cold, and the gentleman being rather disturbed will go down and start his coke fire up very violently. The house will get overheated and there will again be complaints. He will then go down and shut it up tight. Those are conditions of service which are most likely to produce clinkering.

In a magazine feed where the feed is kept up uniformly, it naturally follows that such conditions as that will not occur, that the regulator, if a regulator is used, will be more likely to keep the temperature uniform.

I do not think Dr. Brabbée is correct in saying that this furnace will not produce clinkering with coke. It may not have produced clinkering with the coke he used, but the clinkering you obtain with various cokes differs very materially, and that is one general feature in connection with the use of coke which is needing the most attention. In each district the type of coke should be sold that will be satisfactory for the type of attendance that the householder will give it and householders should not be sold coke which is unsuited to their use.

In the Pittsburgh district, particularly, one cannot but be impressed in watching coke deliveries at the various houses. You see coke being delivered from almost the natural size of the beehive, often as taken from it, to quite small sizes. That both those sizes should be suited to one furnace is, of course, impossible. If satisfactory sales are to be obtained then it is up to those purveying cokes in the various districts to see that the cokes they sell are suitable both in size and quality to obtain satisfied customers.

DR. BRABBÉE: The first question is related to a continuous operation of this magazine feed. Our household is a good example. Last year, especially on Saturdays and Sundays, the boiler was often neglected and the maid complained of the cold. This complaint has ceased. Previously when the valve of the radiator was opened the heat would not come up for half an hour. Now when the valve is opened the heat comes up immediately. This has something to do with the continuous operation of the radiant fuel bed, and also with the presence of dry steam in the magazine boiler.

The second thing was relative to clinkers. Previously, as I said, with good coke in the boiler, we did not encounter any serious trouble with clinkers. Some people coming into the laboratory, seeing the new construction, say, "Why did you put clinker doors in the boiler? They seem not to be necessary."

I tell them there ought to be some clinkering, and therefore we put this large door in to be able to take care of clinkering.

Regarding cokes of different sizes, the coke companies have given us cokes of various sizes and various qualities, and we have not found any great differ-

ence. However, we have used—and we emphasize it—egg and nut size only. We have made tests with pea coke, and although this coke burns satisfactorily, the encountered clinker trouble does not count for the little difference in price. This boiler is especially designed to use coke in egg and nut size.

F. C. GREENE (Old Ben Coal Company, Chicago, Ill.): Has Dr. Brabbée tried to use anything in the nature of soft coal in his furnace? I think I can say to Mr. Nicholls that as respecting clinker formation, Dr. Brabbée takes his secondary air over the fire and there is a less amount of transparency through the ash bed. I do not think that such difficult clinkers will occur in the bottom of the bed where you diminish your air supply through the bottom. That has been our experience in servicing quite a lot of boilers using coke from Illinois coal.

Another point I would like to ask Dr. Brabbée is whether he has tried any low temperature coke in this boiler. We are hopeful of some day in the future turning out screenings which can be made into a very good low temperature fuel, and which, if made at a temperature materially exceeding 500°C., will be found non-clinkering.

DR. BRABBÉE: This magazine boiler can be used for almost anything but soft coal, but there is some hope that the ideas found practical in this construction may lead some day to a soft coal burning boiler of such a type as you desire. We used very low temperature coke in one case which gave no difficulties as far as clinkering was concerned, but the coke was so light that the magazine did not hold out for 8 hours on a 100 per cent load.

MR. GREENE: I think you have mentioned one of the most important features that will be required in a low temperature coke in the future. Low temperature coke is a most desirable fuel but it weighs rather less than nothing. Nobody can be bothered with putting low temperature fuel into a furnace where it requires that person to do continually.

That was one of the problems which we had to solve in our development of a process of low temperature carbonization for our screenings, which amounted in one operation to about 20,000 tons a day. We had to make a fuel which would be as dense, certainly, as the usual coke, if not denser. We succeeded in making a char heavier than the original coal.

DR. BRABBÉE: I would like to say that on different occasions, we have been asked to try special fuels in our test. We have, as far as possible, complied with those requests, because we support everything which tends to give better service to the public.

J. C. HOBBS (Diamond Alkali Company, Painesville, Ohio): May I emphasize the one point that the author made in regard to the distribution of the heating service, by telling you that in some buildings now the heating service is being installed in the floor, giving a uniform temperature? In any building, or any room where there are very high ceiling heights, it is particularly difficult to get a heating on the operating level, on the main operating level, without overheating the upper regions.

P. NICHOLLS: I do not think it would be right to let some remarks made by Mr. Greene go into the record without pointing out their incorrectness. Mr. Greene said that the low clinkering could be explained by the fact that air was admitted over the fuel bed. That is evidently incorrect. The amount of air you admit over a fuel bed depends upon the amount of air necessary to take care of the combustible gases rising from the fuel bed. This magazine boiler is not peculiar in admitting air over the fuel bed. Actually taking the same type of coke, the less air that you do admit through the fuel bed to get a given heat production the more liability there is for clinkering because less air for the same amount of heating will mean that more combustible gases must be rising from the fuel bed which will have to be taken care of by air going in above it. Those conditions of more combustible gases coming off from the top of the fuel bed can be produced by having a deeper fuel bed, or by using a smaller-sized coke.

We have distinct experiments to show that as you use a small coke, and as you therefore put less air through the fuel bed and more over the top to get the same amount of heat, that it will produce temperature conditions in the fuel bed which will give you more serious clinkering than if you used a larger coke and had to admit a smaller proportion of the air over the fuel bed.

MR. GREENE: I only spoke, Mr. Nicholls, of our experience in servicing a great many installations in the city of Chicago for metallurgical coke and for other types of fuels which will clinker. We have found that when you put a considerable amount of the air through the fuel bed you get your clinkering at the bottom. That we practically know. Furthermore, I would like to call your attention to the notable making of clinker with an underfeed stoker, where the underfeed turns to an overfeed, you might say, on the outside of the pile, and the draft all comes through that portion, the temperature rises and you have the fusion to make your clinkering.

EDGAR STANSFIELD (Scientific and Industrial Research Council of Alberta, Edmonton, Canada): I was very much interested in Dr. Brabbée's paper. There are a couple of points I would like to ask in connection with the furnace. One is whether they have developed a warm-air furnace of the same type. I am very much interested in Dr. Brabbée's design of the furnace. Just looking it over it appeared good. I was not quite certain whether he said it was also a hot-water furnace.

I did not understand how the secondary air was regulated. I think it would be advisable for the householder, if the ordinary regulation of the furnace automatically controlled the rate at which the secondary air came in.

There was another point which interested me very much indeed. A good many years ago a large building erected in Liverpool was heated by the panel system, in which the walls are heated rather than the air in the rooms, by the furnace. I think these flat-wall radiators Dr. Brabbée talked about are very much along the lines of this panel system of heating. I agree with the Doctor that anything along those lines is good, and I think will develop rapidly. The only surprising thing is that the system of heating the walls rather than the air has not developed faster. I say "heating the walls" because it is perfectly

obvious these flat panels distributed around the room is a move in the direction of heating the walls rather than the air. The system keeps the temperature uniform and is a step towards comfort rather than condensation. There has been far too much done in the past, especially in testing laboratories and testing buildings, in trying to get some definite temperature instead of comfort. In that connection, I would like to ask Dr. Brabbée whether he has used the Kata thermometer at all as an indication of comfortable conditions, and if so, what results he has had. I have had no experience with it myself but the idea seems good.

Again repeating that there is nothing new under the sun, I believe it was Dr. Nicholls who, when we discussed the panel system of heating the walls and the floors, told me that the old Romans used to do that a good many hundred years ago. More credit to them.

DR. BRABBÉE: This principle of magazine boiler is not applied yet to a warm-air furnace. However, this boiler can be used without any change as a hot-water boiler. The only difference is that the insert pieces in the nipples have to be taken away. You can easily connect an Excelso heater to the steam boiler and also have other attachments for hot-water supply.

The next question was in connection with the regulation. On the boiler underneath the secondary air there are marked points, No. 1, 2, 3, 4, 5. As the secondary air depends on the fuel used and on the rating of the boiler, which is expressed by the boiler lengths, we give in our directions for any boiler lengths and for any fuel, the point at which the pointer shall be.

Regarding the Kata thermometer, we tried to use this instrument but we have not found it successful. In both comparative rooms the humidity was about the same and also the air moisture is equal. Therefore the Kata thermometer is not necessary.

MR. J. BLIZARD (Foster-Wheeler Corporation, New York): There is one thing in connection with this magazine boiler which does not appeal to me. This is the necessity of raising the fuel to a greater height in firing, than it is raised with the ordinary boiler.

I have used all sorts of fuel in the domestic boiler and have found it unnecessary to fire at most more than three times a day, which possibly is less arduous than firing the fuel somewhat less frequently but at a greater height in a magazine boiler.

I doubt very much whether a magazine feed boiler will permit me to fire only two-thirds of the amount of fuel I fire now. I don't know whether this saving we saw in the Bronx really is caused by a cheaper fuel, or whether it is caused by a higher efficiency. But, if I am running, as I think I am, at an efficiency of at least 65 per cent now, the efficiency would have to come up pretty close to 100 per cent to bring the fuel consumption down to two-thirds of its present value. The magazine feed boiler will, of course, be advantageous if it can use a cheaper fuel, such as pea size anthracite, but I am quite sure that you are seeking what I should term, unnecessary complications for houses wherein you get an ordinary good fuel such as coke or anthracite. In addition to that, I do not like the idea of raising the fuel to the greater height in firing.

There is just one other thing I should like to refer to, and that is a point Mr. Nicholls brought up which is not understood as well as it should be understood. The amount of fuel consumed on a grate depends solely on the amount of air you bring through that grate, if the fuel bed is homogeneous. If you are going to increase the consumption of fuel you have to increase the amount of air coming through the fuel bed. Bringing the air over the fuel bed will have no material effect on the rate of oxidization of the fuel on the grate. That is something that has been proved very many times and you cannot get away from it.

Mr. Stansfield brought up a point in connection with this magazine feed boiler as to the method of regulating the secondary air over the fuel bed. Some time ago, at the Bureau of Mines, we ran some tests on that with the ordinary boiler. The interesting and important thing we learned was that with the ordinary boiler you got a tolerable  $\text{CO}_2$  content regardless of how you let the air into the fire pot. In other words, it was a self-regulating boiler which would give you a fair efficiency no matter what you did to it within reason. To my mind that is a very important factor in the ordinary domestic furnace.

CHAIRMAN HUNTER: The next paper to be discussed is one on "Boiler Furnaces for Bituminous Coal" by Professor A. G. Christie.

MR. PORTER: I am sorry that in Professor Christie's paper the lack of time has made it necessary to condense many portions, especially that part presenting the fundamental principles of combustion that are important in connection with boiler furnaces.

Professor Christie, as I read his paper, has taken up these important fundamentals and considered them apparently in the light of the firing of coal on the overfeed principle. It seems to me he has not tied them in as they ought to be, with other methods of firing coal, as for instance, powdered coal firing and the underfeed stoker firing. When coal is fired in powdered form, the air and the coal come into the furnace together, and the decomposition of the coal producing volatile matter, and say, semi-coke, goes on in the presence of air. This is true also of the underfeed fire, but on the overfeed fire, the condition is not the same.

Professor Christie has assumed that a distillation or decomposition of the coal takes place before any air comes in contact with the fuel. This is no doubt true to a large extent in the overfeed fire, but in powdered coal firing and in underfeed firing, we have a different set of conditions, and the steps occurring are probably quite different.

He points out rightly that the volatile products distilling from the coal must be swept away so that the solid can be reached by oxygen and burned.

I would take issue with him, however, in his statement that "air does not reach the coke until the rapid discharge of gases and volatile matter has ceased, unless the air velocity is very high." He brings up here an important fundamental principle of the burning of bituminous coal. Does it distill down to coke before any burning takes place? I think we are justified in believing it does not, at least there is no evidence to show that it does, and there is some,

from studies of coal dust burning, to indicate it does not. The coking process is not so rapid as would be supposed from Professor Christie's exposition of the matter. It involves the time element even more than does combustion. Air and oxygen, even with moderate flow of air and rates of burning in the furnace, reach the solid surfaces while distillation is going on, and mingle with the distilling gases, effecting more and more oxidation of the half-coked material as higher temperatures are reached. The ease of ignition of this semi-coked material is greater than that of the distilled gases.

One very important point in favor of the underfeed method of firing depends upon this very thing, and has not been given enough weight by Professor Christie. This lies in the gradual evolution of the volatiles from the coal in the *presence of air*, (preferably preheated air), as both are brought into the fuel bed together from below. Oxygen, in large quantity, is brought both to the semi-cooked coal and to the volatile products, *as they form*.

Preheated air shortens the flames by effecting more complete combustion of the gases before they leave the fire. The flames thereby are less likely to reach the tube banks, "birds-nesting" of clinker on the tubes is lessened, and a greater heat transfer by radiation results.

For these same reasons, preheat in the air, high velocities of air, and eventually the use of precarbonized fuel on stokers, will make for greater concentration of heat in the fuel bed, and accordingly lesser furnace volumes and high "dollar efficiency" arising from lower costs of plant and attendance.

High velocity of air over the surface of a piece of coal—as can be attained more effectually under stoker conditions than in powdered coal firing,—brings about a scrubbing action which takes away the adhering film of gases and thereby speeds up combustion.

C. A. SELEY (Locomotive Firebox Company, Chicago, Ill.): Dr. Christie's paper states: "The important influence of radiant heat as a means of heat transfer from burning fuel to boiler surfaces, was not fully appraised until within the last few years. This effect is now better understood and all modern furnace designs attempt to take the greatest advantage of radiant heat transfer."

I was interested to note in the previous paper the application of that principle with reference to the domestic furnace. I am a railroad man and I know more about locomotive boilers, while this paper has to do entirely with stationary boilers. In fact, most of the papers have not touched at all on the locomotive problem. Yet there are certain analogies which I think would be of interest, particularly in connection with this paper. As you probably know, there are 70,000 locomotives in the country with a potential capacity of upwards of 100 millions of boiler horsepower. Those boilers are, without exception, with water-cooled surfaces and Professor Christie, advocating for your consideration the connection of this feature in stationary work, speaks of one phase that possibly these water-cooled surfaces might be considered by some as seriously affecting combustion. In other words, have a chilling effect. If proper consideration is given to the question of radiant heat, you will find that his position is thoroughly good.

I have had occasion to ask questions of railroad men at times in order to bring out this point, and we have had a conversation something like this:

"Suppose you are pulling a train on the level and burning about 60 pounds of coal per square foot of grate per hour, what would your firebox temperature be? Would it amount to 2,000°F.?" They would agree that was about the figure.

"Supposing you meet a grade requiring twice the engine effort to get up the hill?"

The answer would be, "I would fire about twice as much coal."

"Would your firebox be twice as hot?"

"Oh, no!"

"Well, you fire twice as much coal and develop twice as much heat, where does that extra heat go?"

You would be surprised at the answers. They very often think that some of it went up the stack, forgetting they had gone up the hill and had the extra evaporation and superheat.

A couple of tests I know of showed that with a doubled rate of firing on the grates of the locomotives there was but 18 per cent increase in the measurable temperature in the firebox. Where the rest of it goes is plainly shown by increased evaporation and superheat and the absorption of the radiant heat in the furnace of a locomotive boiler.

You may think that the locomotive boiler is rather plain and ordinary compared with the complex, stationary designs you have seen on the screen, and yet the locomotive boiler is very efficient, while the overall efficiency of the locomotive generally described is rather low, yet the absorption of heat by the locomotive boiler is shown by the fact that with a doubled rate of coal firing, the variation of heat in the front-end boiler practically absorbs most of the heat offered to it above its own temperature.

R. J. S. PIGOTT (Smoot Engineering Corporation, New York): Gentlemen, the arguments on the improvement of the furnace in modern boilers indicate the need of finding out why it is we do not reach the heat release per cubic foot we did in some of the older installations. A few nights ago Mr. J. G. Worker at a Metropolitan meeting of the Mechanical Engineers, presented a table in the paper he was giving on the rates of B.t.u. releases in a number of installations dating back over fifteen years. The highest one happened to be an installation the writer made in 1913, which was short Taylor stokers, old style, with 19 retorts and hand dumps, under 520 horsepower boilers. The rate of release in the furnace was 158 B.t.u. per cubic foot per hour, maximum. The peak efficiency was 83 per cent, which occurred at a rate of 5,000 to 55,000 B.t.u. per cubic foot per hour. But the efficiency fell off rapidly above that point.

We have been talking of the long flame types of furnace releasing 15,000 to 20,000 B.t.u. per hour with a maximum of 27,000, which implies an expensive furnace. The later installations with full cooled water walls have gone up to 30,000 and perhaps to 50,000 B.t.u. release.

There is one curious fact in connection with all of these installations so far, which gives an interesting plot (Fig. 5). With efficiency plotted against

B.t.u. release per cubic foot, on the long flame powdered coal jobs, curve No. 1, the peak is 83 per cent. The underfeed stoker, curve No. 2, continues this curve, the chain grate, and the overfeed stokers follow on down with the best point for the group at about 15,000 to 18,000 B.t.u. per hour cubic foot. In short, the efficiency of all types lies on practically a single line.

I call your attention to one thing: all of these installations, including the long-flamed powdered coal jobs, have no furnace turbulence. In other words, the mixing is substantially all done before the flame has left the burner. The amount of furnace turbulence occurring in the long flame burner with the air drifting in, is not very great. That is the reason for the length of flame with

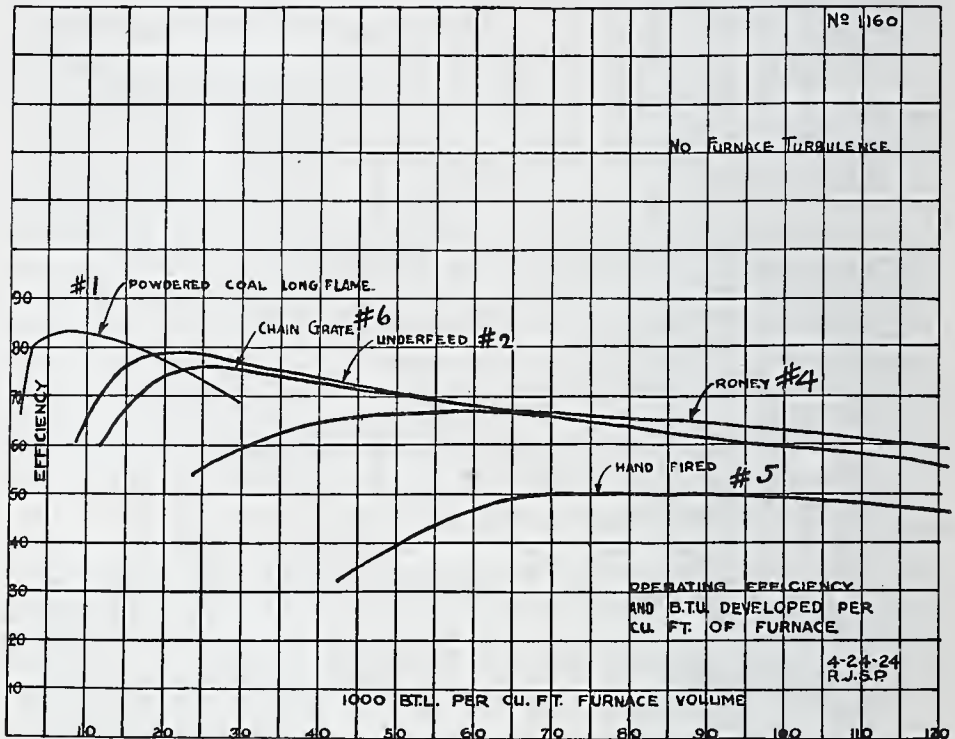


FIG. 5

that type of burner; with the turbulent burner, the turbulence is increased; and if the flames impinge on each other in the furnace, as in tangential or well-type firing furnaces, turbulence is established. Thus the peak efficiency has moved out to about double what it was in all these older installations.

The turbulent burner is providing more mixing at the start, although in most cases the furnace is providing no turbulence.

The question of slag in the boiler proper is one involving three factors, the velocity of gases entering the boiler tubes, the temperature of the gases, and the fusion point of the ash. If slag is to be kept off the boiler tubes the ash must be cooled sufficiently to be non-plastic at the time it reaches the tubes. More and more furnace cooling should be employed as the rates go up. Re-

ardless of whether a bare wall or a covered wall furnace is used, if the furnace is fired at a high enough rate of combustion, plastic ash will form slag on the tubes.

An illustration of this condition is shown in two installations at Kearny, New Jersey. The first installation of 12 boilers, 23,600 square feet each, has full refractory furnaces. As first built the horizontal baffle was on the second tube above the fire. The entry of the first pass is a little over half of the length of the tube. The stokers were equipped with the old standard tuyeres. So much coal was thrown up by the blast action of these tuyeres, (wind pressure was about seven or eight inches at 350 per cent rating) that considerable "popping" was occurring. The velocity in the first pass was so great that a large quantity of the ash was being carried plastic to the tubes. The boiler would plug completely in an hour or two at the higher ratings. The baffle was raised about the sixth tube, increasing the radiant adsorption, and increasing the area of the first pass entry to the full length of the tube. The type of tuyeres was changed to a later design having about 45 per cent more air, which cut down the amount of stuff thrown up into the furnace. As a result of this change the boilers can not go to 350 per cent without any particular trouble of slagging in the tubes. The limit is now the refractory walls of the furnace and not the slagging of the stoker.

The last installation, with the same sized boilers and stokers, is completely water-cooled with bare walls, except for a belt three feet high above the stoker. The object of the cast iron block belt was to cut down the rate of heat adsorption against the hot coal bed, and also to protect the tubes from abrasion by the movement of the coal down the stokers. These boilers have only been running about five or six weeks; so far up to a rating of 300 per cent there is no slag, merely a film of fine gray dust. There is no burning of the blocks except at the base of the front, although the stoker still shows some difficulty with air distribution on one or two rows of tuyeres. That will have to be corrected by attention to air distribution. I think the limits on most of the stoker jobs have been due to imperfect cooling of tuyeres by poor air distribution and refractory troubles. If ratings are to be raised on the stoker, more water-cooling not only will be needed, but it will cause no difficulty if it is employed.

Another curious condition that now shows up, the competition with powdered coal has at last awakened the stoker manufacturer in the last few years to what he has missed. He is beginning to pay a great deal more attention to the kind of furnaces he should get, and to air distribution and cooling. The result is that at the present time modern stoker unburned carbon loss instead of being three or four per cent in average operating results is down within one per cent, so that the margin of advantage of the powdered fuel is not any longer one of efficiency, but of whether or not one is more comfortable in operating, and whether the maintenance bills are lower. The powdered coal equipment up to the present time, including the furnace and the milling operation, has less maintenance than the corresponding stoker in installation. Whether that will still be true or not when more stokers are built with water-cooled walls and preheaters is a question still to be settled.

PROFESSOR WILBERT J. HUFF: I would be very much interested to have information concerning experiments which show that oxygen penetrates the

atmosphere of volatile matter to preferentially oxidize the coke. I gather from what Doctor Porter stated that he knows of such experiments and if so, I would be glad to communicate the information to Professor Christie. I had been under the impression that it is rather difficult for the oxygen to reach the coke particle until the gaseous atmosphere had been swept away by a high air velocity.

PROFESSOR HOBBS: There is one principle that I think might be emphasized somewhat, and that principle is the cooling of the gases as far away as it is necessary from the tubes to prevent the slag from becoming a real nuisance. I have in mind a case where slag was a serious limiting factor. This happens to have been in connection with some straight tube boilers. The conditions would become so bad that the bottom row of the tubes were plastered over almost as completely as an ordinary wall is plastered by a \$14 a day plasterer. The solution to that was more in the nature of a remedy than a prevention, although it turned out that the actual remedy was not only a prevention but it also assisted in other respects which I will mention later.

In this case we used a conventional straight tube boiler. One half of the tubes in the straight tube installation were removed, making alternate tubes. The thing that was needed was distance between the tubes laterally in order to prevent slag. The whole thing was designed originally in order to prevent slag which built up from arching across. Actually the slag when it did come soon built up. The tubes remained clear. There was not any accumulation on the bottom row of tubes.

We were very much surprised the rating of the boiler had been increased. That brought up a point which I am sorry Professor Christie is not here to discuss, that is, as to the effect of radiation on a coal surface. We have here the expression used in every paper to which I have listened, that the projected area of coal surface was the index of heat absorption. If we will use the light analysis and assume that heat behaves in the same manner that light does, projected area is not necessarily the index to radiant heat absorption.

In order to explain why the rating was increased in this particular case, a graphic analysis was attempted by which we marked the different surfaces that were exposed to radiant heat. We found that after the change was made a number of the surfaces were receiving radiant heat from different directions. Apparently, that has some effect at least in increasing the capacity which was raised from 5 to 10 per cent of the rating of the whole installation.

I am not attempting to tell you why this radiant heat theory acts this way, but it seems to act that way and I would like very much to have an explanation. In general, I reach this conclusion: Those of you who have worked with steam condensers can picture the development which has taken place in the arrangement of tubes. I have been in stations within the last year in which a great many tubes have been removed from the condensers with a benefit, an increased capacity of increased vacuum, because the steam was allowed to reach the condensing surface. I have not yet heard of any boilers in which these tubes have been removed to allow the radiant heat and gases to reach the tubes quicker, but it seems to me that we will come to a change in boiler design some day that will allow more radiant heat to be absorbed from the top part of the

furnace. The change in boiler design will not necessarily affect the combustion as much as going to the coal surface.

Mr. Pigott pointed out a refractory surface just about the stoker which was used in an installation mentioned, and I believe we all would like to have some refractory at the point of combustion. After combustion is complete then the problem of cooling the ash so it does not stick to the tubes I think could be done more by surface in the latter part of the furnace.

MR. NICHOLLS: I will not attempt to answer Mr. Hobb's question, but would it not be better if he stated the meaning of his terms more distinctly? He said the heating was increased. His rating might have been increased because he was able to burn fuel at a higher rate without getting a shutdown due to accumulation of slag. In this question of the amount of radiation is the point of whether he got an improved thermal-efficiency from his boiler tubes, that is, whether his bank of tubes absorbed heat better, and produced a lower drop in temperature. That his rating increased may have nothing to do with the radiation, but only show that he got an improved efficiency at the same rate of burning. Whether he got a big enough temperature from the entrance of the gases to the tubes to the exit would be rather a question he would have to state clearly before his question would be considered legitimate and to the point.

PROFESSOR HOBBS: I will state it in this way: Operating at the same rating, the stack temperatures were 40° lower than previously. From a practical standpoint, when the first installation was made the fireman said it was no good because the fire was not burning properly. They noticed it immediately and called attention to the fact that the furnace did not look hot, notwithstanding the fact that the steamheater showed an increase. I believe that is the best information I can give you on that point. Not only were we able to increase the rating, but if we wanted to operate the same rating the increased efficiency would effect a lower slag in the lower furnace temperature; in fact, I would like to know some way to measure furnace temperature, and I would like to have a comparative method of stating it.

MR. NICHOLLS: I would suggest that there need not be consideration of change in radiation as far as these tubes are concerned, but that the question is answered either by the explanation that he obtained better heat transfer in the bank of tubes, or that he prevented clinker accumulation on the face of the tubes and left them open to receive radiation with a resulting increase in efficiency.

PROFESSOR HOBBS: Would the furnace temperature be decreased with the tubes clean in the original condition?

MR. NICHOLLS: It would be. The tubes would receive more radiation because they were not hidden by slag.

R. S. McBRIDE (Assistant editor of *Chemical and Metallurgical Engineering*): The chemical engineer's interest in coal has been primarily as a raw material

for the processing industries. However, quite lately the chemical engineer has been giving thought to some rather unorthodox ideas of coal as a source of power. Within that field he sees the same type of intensive economic competition between steam-electric and hydro-electric properties as prevails within his accustomed field between competing methods for manufacture of a wanted commodity. The fact that energy and not commodity is the end product does not in any way lessen the competition.

In viewing this field of energy supply the chemical engineer has noted the fact that large power stations are attaining average over-all efficiencies with steam-electric systems around 25 per cent conversion of heat in the coal to electricity on the bus bar and in one or two instances reach a maximum of 28 per cent. Thermodynamic considerations indicate that until the chemical engineering profession furnishes better materials of construction the mechanical engineer dare not go to much higher temperatures or pressures. The chemical engineer does not despair of supplying better structural materials, but he also asks the logical question, "Is there not some other material than water which has preferred thermodynamic properties and which would permit, let us say, 40 or 50 per cent over-all efficiency in energy transfer from coal to electricity without increase in temperature or pressure in the boiler?"

Some years ago the mercury boiler which was suggested by this possibility was proved by careful mechanical engineering development to be a technologic success and since then several successive boilers have run on commercial load. A large unit will soon go into service at South Meadow Station, Hartford Electric Light Co. The chemical engineer, however, would not view with satisfaction the choice of such new boiler medium as mercury. That commodity is obviously an wholly inadequate supply even though we were to utilize all known sources of mercury to a maximum. The chemical engineer, therefore, suggested in very recent years that di-phenyl oxide, an organic chemical not difficult of production, should be used instead of water or mercury. Very much more recently, the closely related chemical material, di-phenyl, has been suggested as perhaps of even more nearly perfect boiler behavior.

Already several very interesting quasi-industrial or full plant-scale trials have been made with this type of boiler medium. The results are not yet convincing, but they are sufficiently encouraging to warrant optimism. The chemical engineer is today probably almost ready to assure the mechanical engineer that he will furnish a boiler medium affording not less than 40, and probably nearly 50 per cent thermal efficiency even when operating within the present pressure and temperature limits. We cannot yet say just what conditions of plant or of power requirement will make these advances both technically and economically successful. It appears, however, that there is warrant for optimism. The cost of such boiler medium certainly is not excessive. Its life and behavior in the boiler are apparently good. It can be made in unlimited quantities; and fortunately, the greater the market requirement the lower is the probable future cost—quite a contrast to mercury.

It would be presumptuous at this time to make any effort to forecast the replacement of steam-electric power by some other chemical-electric power system. It is, however, none too soon to consider what would be the effect

of such substitution when it becomes economically possible. Suppose, for example, that we were to obtain the prophesied 40 per cent over-all efficiency. Immediately, one sees that for a given power requirement the coal consumption would be but half that with present steam-electric systems. Presumably such plant and its new boiler medium would cost somewhat more than the present steam-using plant. But if the fuel bill were cut in half, a substantial increase in capital charges would be more than warranted. Furthermore, such increase in fuel economy would place this new electric plant in a much more favorable competitive relation to hydroelectric properties. Even to-day, with high steam-boiler efficiencies, it is often cheaper to generate the requisite power from coal than to bring it substantial distances from water-power properties involving high investment costs. How much more certain it is that we should have a cheap fuel-made power where and when desired if we should go to these new methods about which the chemical engineer is beginning to talk.

In all these comparisons, whether they be related to power, to coke, to gas, or to other coal products, the chemical engineer seeks, if he be wise, to move forward by short and sure steps. He asks that any new scheme of carbonization, any new process for low temperature coking, any new unit machine, any new material proposed as a boiler medium, shall stand the test of commercial trial over a considerable period before he will advocate its wide-spread adoption. Most of all the chemical engineer demands that any new machine, process, or material, shall produce the desired product, whether commodity or energy, with profit. He regards any new advance in science or technology as poor chemical engineering until it will yield to its backers increased financial advantage. He believes that the making of products without profits is futile.

## LOCOMOTIVE FUEL

By W. L. ROBINSON

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The supremacy of high rank bituminous coal as locomotive fuel is based upon the wide general distribution of the deposits, the ready accessibility for mining at low cost and the high average heat content of the fuel.

The commercial mining of bituminous coal is carried on in twenty-nine of our States, though more than 90 per cent of the total production comes from three important areas, the Appalachian, the Eastern Interior and the Western Interior.

From these extensive regions bituminous coal moves out for use as locomotive fuel until the length and cost of haul brings it into competition with the great petroleum deposits of the southwest and the Pacific coast region.

Each of the railroads naturally draws its fuel supply from the coal of the required quality produced in the most convenient and favorable location with reference to cost at the mine, cost of haul and cost of distribution to coaling stations.

Railroads located in the coal producing regions and drawing traffic from the mines are particularly fortunate in being able to obtain their fuel at low cost of haul and distribution, a portion of it being taken direct from mine tipples onto locomotive tenders.

Ninety per cent of the locomotive fuel of the railroads of the United States is bituminous coal. Fuel oil used in the western territory remote from adequate coal deposits makes up the bulk of the remainder.

With an average annual production of somewhat more than a half billion net tons of bituminous coal during the past five years, the average annual consumption as locomotive fuel has been 126 million tons or in round figures about one-quarter of the total, and a considerable tonnage of our exported coal is used for the same purpose by our neighbors.

In one respect the railroads are intimately associated with the production of bituminous coal even aside from railroad ownership or control of coal land.

More than 50 per cent of the revenue tonnage of the railroads consists of products of mines, the bulk of which is bituminous coal and coke, and it has been estimated that the railroads have more money invested in facilities for transporting coal and coke, than is invested by the coal producers themselves in operated coal mines and their equipment. More than 50 per cent of the railroad non-revenue or company material tonnage is fuel, of which about 20 per cent is used in the movement of passenger trains, 5 per cent for miscellaneous purposes and the remaining 75 per cent in assembling, hauling and distributing freight tonnage of which the biggest single item is revenue shipment of bituminous coal and coke.

Fuel is by far the most expensive single material purchased and used by the railroads. Fuel expense stands second only to wage expense in railroad operation.

It might be said that the railroads purchase fuel and from it manufacture the transportation which they sell, just as the central power station transforms the fuel value of coal into marketable electric power.

The importance of the item of fuel expense in railroad operation and the abundance of high rank bituminous coal widely distributed and produced at relatively low cost, explains in part, at least, the fact that the railroads endeavor to secure good quality high rank coal which they consume as fuel in the raw state. The main consideration is the necessity, imposed by the restrictions under which they operate, of producing the maximum amount of transportation for the minimum fuel expense. It is therefore reasonable to anticipate that the railroads favorably situated to do so will be among the first power producers to take advantage of the opportunity to use processed fuel of suitable characteristics when this industry has demonstrated that a regular supply in adequate quantity is available at a cost which will permit the cheaper production of foot-pounds at the locomotive drawbar.

The choice of locomotive coal is affected by other considerations than the simple ability to get locomotives from beginning to end of their runs. Most essential of all is the consideration that the fuel of a locomotive shall be of such quality as to render remote the possibility of delay and interference with the movement of other locomotives and trains on the road at the same time.

Under present average conditions it requires about one-half a ton of coal to start a freight train and bring it up to running speed after a

stop on line of road, so that elimination of stops and delays in the movement of trains is one of the important factors in the reduction of fuel expense. Every railroad operating officer can recall from his experience occasions when all other considerations have had to be subordinated to getting the trains over the road.

The use of fuel of such quality that it causes no operating difficulties places the organization in position to take full advantage of the refinements in operating practice which produce the best economy in fuel utilization.

One of the most promising modifications of conventional practice observable at the present time is the extension of the length of run of locomotives, that is, the service mileage made before lay over for terminal attention. In many instances this practice results in better utilization of the individual locomotive and the possibility of reducing the number of locomotives for a given volume of business with obvious economy from the standpoint of employment of the capital investment in locomotives.

From the angle of operating feasibility the condition of the fire is the principal limiting factor and the extension of the practice, with elimination of intermediate terminal attention, less grate shaking on the run, less dumping of ash pans and fire cleaning, freedom from dirty flues, slagging of heating surfaces and related difficulties, depends to a quite material extent upon the provision of clean coal without an excessive proportion of fine sizes.

#### COMBUSTION IN THE LOCOMOTIVE FIREBOX

Limited space—particularly as to height and width—is the principal difficulty with which steam locomotive designers are confronted in their endeavor to improve locomotive fuel economy.

Limited grate area makes necessary extremely high rates of combustion in order to develop the capacity required to realize maximum efficiency in the locomotive as a transportation machine unit and the strong draft which must be used to support the high combustion rate combined with the unavoidable restriction of firebox volume makes impossible the provision of ideal combustion conditions such as may be obtained in stationary steam plant practice where no space limit is imposed.

After all the improvements in steam locomotive design which the future will undoubtedly bring forth, the conclusion is unavoidable

that a wide disparity will still remain between the efficiencies of stationary plants and locomotives.

The average distribution of the heat in the coal fired to a locomotive of conventional design, representative of the greater proportion of the locomotives now in service, assuming that the locomotive is in perfect mechanical condition and skillfully fired and operated has been stated by competent authority to be approximately as follows:

	<i>per cent</i>
Loss to ashpan.....	4
Loss by radiation.....	5
Loss to heat in burned gases.....	14
Loss to unburned gases.....	4
Loss to cinders.....	8
Loss to locomotive friction.....	1
Heat in exhaust steam.....	<u>52</u>
Total lost and rejected.....	88
Used by steam auxiliaries.....	6
Applied as work at drawbar.....	<u>6</u>
Total.....	100

It will be observed that more than 75 per cent of the heat of the coal is rejected at the stack. In recently designed locomotives commendable results have been obtained in reduction of this loss by more efficient transfer of heat to the steam, more efficient use of the steam in the cylinders and recovery of heat from the exhaust steam to heat the boiler feed water.

#### VOLATILE CONTENT OF LOCOMOTIVE COAL

The rise and fall of a railroad line due to variations in gradient between such limits frequently experienced as from level track to 2 or 3 per cent of slope introduces the condition of continuous change in the power output of the locomotive and in the demand of the engines for steam. The varying demand for steam is relayed to the firebox and registered in widely changing rates of combustion on the grate. The desirability of realizing the maximum hauling capacity of the locomotive on the ascending gradients makes it advisable to use a quick burning fuel which immediately upon introduction gives off its gases, high in heat content, thus permitting the forcing of the fire at the critical points of the run. Other factors being equal, the higher the volatile or gas content of the coal the more suitable will it be found for locomotive fuel. The practical value of maximum steam capacity

over-balances the reduction of fuel efficiency resulting from the high rate of combustion of high volatile fuel in a firebox of restricted volume, and with the use of a good brick arch, a careful fireman handling his fire so that only a gray haze shows at the stack can maintain good average fuel efficiency with high volatile coal.

#### GRADE OR SIZE OF LOCOMOTIVE COAL

The draft intensity of locomotives is extremely high as compared with that of stationary steam plants. The maximum draft at the stack may be 10 inches of water or more with an average of 4 to 6 inches which will correspond to around  $1\frac{1}{2}$  inches in the firebox. Such high draft carries out as unconsumed carbon on the average of 6 or 8 per cent of the fuel value of the coal fired onto the grates and a small increase above the critical percentage of fine sizes or slack in the coal as fired, will result in a very large increase in the percentage of stack loss.

Road tests of stoker fired locomotives based upon entire trips involving low as well as high rates of combustion have shown, on the basis of equivalent evaporation, an increase of 20 per cent in consumption of 2-inch screenings as compared with run of mine and an increase of 25 per cent in consumption of  $\frac{3}{4}$ -inch screenings as compared with the 2-inch screenings. This illustrates very clearly the vital importance of limiting the content of fine sizes and slack in the coal as fired.

Some variation in the proportions of the different sizes, the maximum and minimum sizes and the resultant average size of the coal as fired is required, to assure maximum economy in utilization in each of such widely varying kinds of locomotive service as hand-fired switching locomotives, accommodation passenger trains, through heavy passenger trains and stoker-fired heavy freight and passenger trains. In general, it appears to be the consensus of informed opinion that the single grade best adaptable to such variations in service requirements is the run of mine coal without lumps in excess of 6 inches maximum dimension and with not more than 25 per cent content of  $\frac{3}{4}$ -inch screenings.

#### ASH CONTENT OF LOCOMOTIVE COAL

The non-combustible content of locomotive coal plays a very important part in the fuel performance. The moisture is so much

inert matter purchased at the same price as combustible and requiring about 0.1 per cent of the heat content of an average coal to raise each 1 per cent of moisture to stack temperature. Of much greater significance than moisture is the ash content, because of its possible effect upon the rate and efficiency of combustion. Non-clinkering ash is not troublesome and only represents so much inert matter. Ash which clinkers under the conditions of combustion in the locomotive firebox obstructing the air supply through the grates and possibly causing damage to the grates through overheating them, may result in any degree of trouble from merely inefficient combustion to complete steam failure.

Slagging of heating surfaces in the conventional locomotive firebox is closely related to the slack and ash content of the coal and the character of the ash. The intense draft carries a considerable percentage of ash and fine sized cinder to the flue sheet through the high temperature zone of the firebox. If the ash becomes plastic at the temperature experienced, part of it sticks to the sheet and builds up accumulation of so called honeycomb which in extreme cases blocks the flues.

The results experienced from early attempts to use pulverized coal obtained from miscellaneous sources, in the conventional locomotive firebox, were discouraging largely because of excessive slagging of the flues, and clearly demonstrated one of the serious difficulties that may be expected from too high a proportion of fine sizes in coal fired on locomotive grates, if the ash has a low fusing temperature.

The mechanical stoker, required to develop the capacity of locomotives of more than 50,000 pounds tractive effort, crushes the coal to a size not exceeding two to three inches maximum dimension. This crushing as the coal is delivered to the firebox increases to some extent the proportion of the very fine sizes, and the resultant increase in cinder stack loss has become a serious problem in heavy through passenger service on some roads. Improvement of this condition is anticipated through the effective coöperation extended by the stoker manufacturers in modifying their construction and in the provision of coal with a reduced proportion of fine sizes.

#### PREPARATION OF COAL AT THE MINE

It is impossible to overemphasize the value to coal consumers of the best practicable degree of preparation of coal before shipment, to

insure close correspondence between the quality of the coal as shipped and the prepared seam sample upon the basis of which the sale of the coal is usually made. It is a very common occurrence to find shipment samples showing a larger ash content than even the unprepared seam sample from the mine due to the failure to properly handle bad roof or floor conditions.

A difference of only one per cent between the ash content of prepared seam sample and shipment sample is of such ordinary occurrence as to attract only casual notice, but let us illustrate the importance of this variation to our railroads alone, as coal consumers. One per cent is equivalent to 20 pounds per ton. Our railroads use in round numbers 125 million tons of coal per year. Twenty pounds of extraneous material in each ton of this annual consumption amounts to one million and a quarter tons which if loaded into 25 thousand 50-ton capacity coal cars would make up 213 trains each a mile long. End to end the cars would reach from Pittsburgh to Cleveland and 65 miles beyond. This waste material is not only paid for at the average price of the fuel but is hauled to consumption points loaded onto tenders where it imposes a further handicap upon combustion efficiency and fuel economy, and finally has to be hauled away from ash pits, a total loss from beginning to end.

#### SUPERVISION FOR LOCOMOTIVE FUEL ECONOMY

After selection of the locomotive coal has been made, based upon consideration of the factors previously mentioned and possibly some others of a purely practical local application, economical utilization can only be secured by competent, comprehensive and continuous supervision over such details as those mentioned following:

*a.* The inspection of the coal at mines, in yards, at coaling stations and on locomotive tenders to insure that the standards of preparation are properly maintained by the producers.

*b.* The handling of the coal from cars to locomotive tenders to minimize the degradation and the separation of sizes.

*c.* The distribution of the coal from mines to specified coaling stations and disbursement to locomotives so that each coal will be used in the class of service in which it will produce the most satisfactory results.

*d.* The maintenance of good operative condition of the locomotives through reports to the shops and engine houses when repairs occasioned by even minor defects are required.

*e.* The education of the locomotive engineers and firemen in the practical application of economical principles to the details of their handling of the locomotives in their charge.

*f.* The various factors involved in securing the interested coöperation of the personnel in all branches of the railroad organization and coördinating their efforts toward improvement in train loading, train dispatching and movement, the elimination of delays and the many other details which affect efficiency of performance.

*g.* The records and reports upon which distribution of fuel charges is based and by which the performance is determined and the compilation and distribution of adequate statistics for the prompt information of all concerned as to the trend of the current performance and the reasons therefor.

During the past two decades, the managers of our most progressive railroads have developed the realization that the possibilities for saving money in the operation of the properties, through improvement in the economy of fuel utilization, fully justify the maintenance and support through lean years as well as through prosperous periods of more or less extensive special organizations whose activities are devoted to the supervision and coördination of the various factors involved in economical utilization of the locomotive fuel and of the fuel used for miscellaneous purposes as well.

To those particularly interested in this phase of the subject, a review of the published proceedings of the International Railway Fuel Association would prove informative as to progress made from small beginnings on a few roads to the present extensive development on many roads.

Briefly the usual plan provides a central bureau, the head of which reports directly to the chief operating officer. The bureau usually exercises staff supervision over the distribution of the fuel from mines to locomotive coaling stations and the consumption points of miscellaneous fuel, over the compilation of the detailed reports and records of fuel used, as separated between the various classes of service and over the issuance of statistics of the current performance. It endeavors to coördinate the fuel economy program with the related features of the work of other departments which handle such details as the fuel purchasing, inspection and accounting. It works with the road locomotive supervision to insure the maintenance of standard practices in the operation of locomotives, and in the instruction of the locomotive engineers and firemen as to the many details of their work

which affect the fuel performance. The reporting to the shop supervision of the operative condition of the locomotives from observation of performance in service of individual locomotives and the follow up to insure that repairs are made is an important function of the staff of the fuel economy bureau.

On our roads which are really organized for fuel economy, the old time "traveling fireman" a mighty man with the coal scoop, fire rake and grate shaker, whose job was to get to the "cripples" whether mechanical or human as they might develop in the days work on his division and straighten them out or bring them in, has been succeeded by the modern Fireman Instructor or Instructor in Fuel Economy, assigned to the division or district of each Road Foreman of Engines, whose duties are—to ride and inspect locomotives, observe the handling and firing of the locomotives, instruct the engine crews where necessary in correct methods of handling and firing, report power conditions, give attention to the methods of cleaning, banking and preparing fires in locomotives and the coaling and handling of the locomotives while in the charge of engine terminal employees, and in general to endeavor to bring about every practicable improvement in the detail conditions which affect economy in the use of locomotive fuel.

These men are selected from the ranks of the best young promoted locomotive engineers after having demonstrated special ability in their chosen work and the possession of the qualities of character and personality which fit them to be instructors and directors of their fellows. It is their important function to forestall locomotive failures and uneconomical practices by educational methods applied and demonstrated on the footboard and at the throttle and in due time their activities develop primarily into preventive rather than remedial channels.

#### IMPROVEMENT IN LOCOMOTIVE DESIGN

The development and use of a gradually increasing proportion of locomotives of greater capacity and better design, has contributed to an important extent to the improvement in economical utilization of locomotive fuel during the past 15 or 20 years. While there are still in service many locomotives of the old types built 20 or 30 years ago, an increasingly large proportion of them are being rebuilt to an approximation of recent standards of design and equipped with

proven economy producing appliances, and each year sees many of the obsolete type retired and replaced by new locomotives of modern design, with resultant beneficial effect upon the performance averages.

The future holds much of promise in the direction of further improvement in steam locomotive design. Boilers of new design, probably of the water tube type, with ample grate area and greater firebox volume promise better evaporation rates, possibilities of much higher steam pressures and lower maintenance costs. Refinement in engine design and improvement in mechanical construction and provision for lubrication will be accompanied by better steam rates, increased stability in the adjustment of parts subject to stress and wear and lower maintenance costs.

The reduction of standby fuel loss in coal fired locomotive service is a goal hopefully regarded by all railroad operating officers. This is one of the principal advantages derived from the use of oil as locomotive fuel, and the equal flexibility offered by pulverized coal has encouraged engineering research which gives promise of eventual success in the application of this method through modification of firebox and boiler design and the provision of adequate volume of combustion space. It is estimated that approximately 15 per cent of the total locomotive fuel is consumed in cleaning, maintaining and preparing fires while the locomotives are in the engine terminals, in addition to which, are the standby losses on line of road. This represents a quantity equivalent to 15 or 20 million tons of coal per year on our railroads. The saving of at least one-half the normal standby consumption on each locomotive equipped is conservatively to be anticipated from the successful utilization of pulverized coal, a possibility which it is considered fully justifies the extensive research devoted to the problem and the confidence of railroad officers in its final successful solution and general application. The importance of this consummation in the provision of another outlet for the utilization of the fine sizes of coal is not to be minimized by the coal operator and the industrial consumer of bituminous coal. Meantime, at some of the large new engine terminals, where the investment in the required facilities can be justified, there appears to be prospect that standby fuel saving, with the elimination of objectionable smoke, may result from the use of the process of direct steaming of coal burning locomotives by raising boiler pressure with steam supplied from the stationary boiler plant.

## IMPROVEMENT IN COAL AS SHIPPED

Of equal if not greater promise with respect to lower rates of fuel consumption per unit of work performance is the prospect that more competitive conditions in the production and sale of bituminous coal will force concentration of production into the operations better favored by nature in the character of the deposits and the quality of the coal and will force those who are to survive to adopt the best available mechanical equipment, to mine and convey the coal from working face to railroad car with a minimum of degradation consistent with permissible production costs and to remove extraneous material from the final product, and thus reduce its ash content to the minimum economical limit and correspondingly improve its thermal value.

It is well known that by far the greater number of bituminous coal mines are not yet equipped, even with facilities for hand picking the coal. At many operations the coal is simply dumped down gravity chutes of greater or less length to the railroad car, each mine car dump landing, after a lump-shattering free drop, in a heap which effectually conceals most of the extraneous material from the view of the man who is sometimes stationed on the car to remove the larger pieces of foreign material. Under such conditions it is perfectly natural that the importance of having the miner clean the coal before loading at the working face should be stressed, since if it is not cleaned in the working place it will not be cleaned at all.

It is distinctly encouraging to the coal consumer to find that many coal operators are now seriously considering the installation of such of the available facilities for better preparation as promise to fit their individual problems, taking into account the possibility of reducing the cost per ton of production with improvement of quality and resultant stability of sales.

For some operations justification can hardly be found for anything more elaborate than screens to separate the sizes so that it is feasible to see and hand pick the impurities on separate picking tables, and loading booms to eliminate the degradation due to the existing free drop from chutes to railroad cars.

Larger producers with ample acreage in reserve for future development are studying and experimenting with more elaborate systems of mechanical loading, conveying, mechanical cleaning on the flotation principle and the marketing of separated sizes, adapted to particular uses. The mechanical cleaning of screenings and the sale of this

product for metallurgical or other similar uses for which coal must be sized down, by crushing or pulverizing, offers encouragement of the possibility that at a larger number of operations locomotive fuel containing only the desirable proportion of fine sizes, may soon be made available.

It is probably too early in the development of mechanical cleaning apparatus to offer any very definite conclusions as to the comparative desirability of the various methods, each of which may be no doubt particularly adaptable to the conditions under which it has been developed. In the northern parts of our coal producing territories, the present tendency appears to be to favor the principle of air flotation in the coal cleaning equipment. Factors involved in the choice are the difficulties of suitable water supply at many mines and the cost of pumping and circulating the water, the freezing of the product in the railroad cars during the winter season and the increased moisture content of the coal.

## CARBONIZED FUEL—HOW WILL IT BE BURNED?

*By* M. ALPERN

*President, American Engineering Company, Philadelphia*

*Read by J. G. Worker, Assistant to the President, American Engineering Company, Philadelphia*

Into the economy of steam making at central power stations many factors enter. Besides fuel cost and fuel efficiency, there are factors having to do with overhead and operating expense, the fixed charges of the plant, that are equally important. These are influenced by the type of fuel used.

Carbonized fuel suitably prepared by methods designed for the purpose, may have certain burning characteristics that influence favorably these items of fixed charge and operating expense. For example, they will tend to lower the installation costs by lessening required furnace volumes, are likely to lessen fixed charges by improving the capacities attainable with high efficiency, and may lower the labor cost and repairs and replacements by increasing the smoothness and steadiness of operation.

These factors appear to offer possibilities of supplementing the gains derived from by-product recoveries and improved furnace efficiencies, to a degree that may eventually counterbalance the costs and losses and save the day for pre-carbonization at power plants. They have not yet however been fully demonstrated.

By the recovery of oils and gas worth \$1.00 to \$1.75 per ton of coal, it would seem that the costs of carbonizing, with simple apparatus and utilization of all possible waste heat, could eventually be more than covered. There would remain the economies above noted in furnace cost and operation to be developed, so as to counterbalance a substantial part of the loss of 25 to 30 per cent in total available heat units undergone in carbonization. In other words, the prepared fuel, enhanced in value by these factors, but less in quantity than the original coal, must exceed in effectiveness the coal from which made.

In any event the margin to be obtained in such operations, as applied to boiler furnaces, is bound to be small, unless surprising increases shall occur in the market values of by-products. For this reason, a large turnover of fuel is required, and plant units of large

capacity, with steady operation on full loads. Central stations taking care of the base load in an interconnected system, no doubt, best fulfill these requirements.

But as Orrok has noted,<sup>1</sup> a power station using turbines drops off even in as short a period as five years to such a lowered capacity factor that it becomes unsuited for carrying the base load in an interconnected system. The steady load would economically be transferred to a newer plant. At such a time, therefore, carbonizing auxiliary plants could no longer be operated at full load and highest efficiency. Although this constitutes a real drawback to full and most economical development of carbonization at power stations, it does not prevent the economical application of such pre-treatment to a certain number of the boiler units at any base-load station, that is, to a percentage of the full load such as is likely to be demanded over a period of years corresponding to the probable life of the carbonizing equipment.

Increasing coordination in control of gas and electric utilities, together with growth of the central station idea, will afford opportunity for development of carbonization auxiliaries at power stations. Gas plants supplying city gas, particularly those having equipment for blue water gas or producer gas manufacture, can make good use of the rich gas arising from low temperature carbonization, for admixture with the leaner water gas or producer gas, for enrichment. It is low-temperature carbonization, rather than high, that appears best adapted to the preparation of boiler furnace fuel. Its gas has a heating value of 700 to 900 B.t.u. per cubic foot, and as an enricher should be worth at least 30 cents per thousand to the gas company (\$.75 to \$1.00 per ton of coal carbonized).

A large public utility combining gas and electric production, and possibly operating both in one station, would be in a position also to refine and market directly the oils and tars produced in the carbonizers, establishing its own selling organization and keeping at a minimum the marketing expense. Important developments in the application of oil fuels in internal combustion motors may be looked for, with a tendency to increase the marketability and price of the heavier oils.

What we have outlined in the foregoing presents low-temperature

<sup>1</sup> Geo. A. Orrok, *The Economics of Coal Carbonization*, *Jour. Amer. Soc. Mech. Eng.*, June, 1927.

carbonization in more or less of a new light, giving up the idea of high-priced marketing of the coke to domestic users, and depending rather

TABLE I  
CHARACTERISTICS OF LOW TEMPERATURE COKES

	MOIS- TURE	VOLA- TILE MATTER	FIXED CAR- BON	ASH	B.T.U. PER POUND (DRY)	SPECIFIC GRAVITY (BULK)
Coal used to make Sample A.....	1.7	39.7	49.7	8.9	13,700	1.3
Low temperature cokes:						
Sample A .....	3.0	13.6	70.1	13.3	12,700	0.85
Sample B .....	1.9	24.0	65.3	8.8	13,000	0.77
Sample C .....	1.9	14.6	69.1	14.4	12,419	0.72
Bureau of Mines*.....	0.6	9.1	81.6	9.0	12,870	
British Fuel Research Board ..	0.5	8.4	79.3	11.9		
Coalite (British).....		10.0	83.6	6.4		
Nielsen (British).....	1.9	11.5	70.7	15.9		
Representative†.....	2.2	7.6	80.5	10.6	12,758	
High temperature cokes:						
Beehive‡.....	0.7	1.7	86.7	10.9	12,715	
By-product‡.....		1.6	88.1	10.3	12,730	0.95§

\* From Utah coal, at 1,380°F., Reports of Investigations No. 2278.

† Gentry, Technology of Low Temperature Carbonization, p. 130.

‡ Bureau of Mines, in Report Carbonization Com., Amer. Gas Assoc., 1926.

§ Approximate average of several samples.

TABLE II  
REACTIVITY OF COKES (BUREAU OF MINES)

	REACTIVITY INDEX*			KINDLING TEMPERA- TURE†
	In air	In carbon dioxide	In water vapor	
Low temperature coke‡.....	72.4	62.5	29.0	°F. 266
Gas Works Coke "R".....	65.4	6.0	13.9	554
Gas Works Coke "B".....	62.8	3.3	10.2	608
By-product oven coke.....	63.7	4.6	11.2	590
Beehive coke.....	61.2	3.0	10.2	600

\* Percentage of the theoretical maximum of carbon gasified.

† Temperature at which carbon dioxide is first formed in air.

‡ Sample prepared at 1,380°F. in superheated steam.

on the value of a steady, continuous coke disposal outlet free from the burden of re-handling and transfers, preparation cost and losses, and

particularly the heavy item of selling expense. We are calling attention especially to the gains likely to be realized from lessening of power plant fixed charges and operating costs by use of such fuel as compared to raw coal. This is a feature we think has not hitherto been stressed, and while the gains may not prove to be large, they may well be sufficient to turn the balance in favor of the proposal.

On the composition and physical character of low-temperature coke, there are data at hand. It is a light, porous material, having a

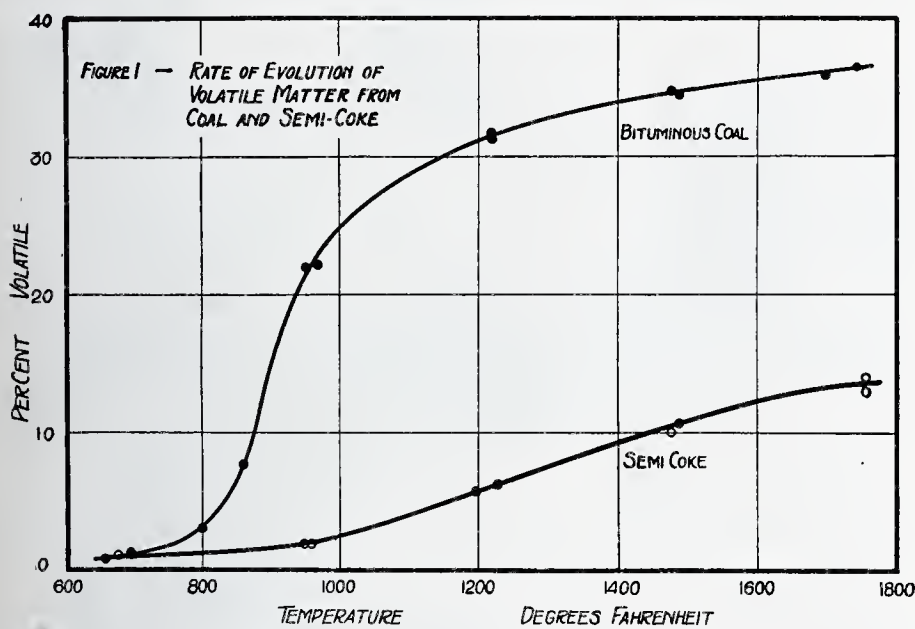
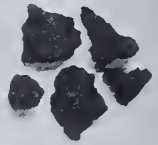


FIG. 1. RATE OF EVOLUTION OF VOLATILE MATTER FROM COAL AND FROM SEMI-COKE

low ignition temperature as compared to ordinary high-temperature coke, and a high combustibility rate. It carries 10 to 20 per cent volatile matter, (none of it smoky in nature), and has a heat unit value somewhat lower than that of the coal from which made. In Table I, A, B, and C are samples obtained by our laboratory from trial operations of different processes on a commercial scale, two in America and one in Germany. These cokes were not manufactured with any purpose of applying them to use as boiler fuel. From coke "A" there had been obtained 30 to 31 gallons of tar per ton of coal carbonized.

Untreated



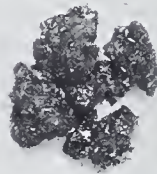
610° F.



740° F.



860° F.



1100° F.

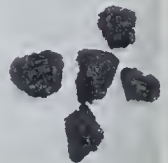
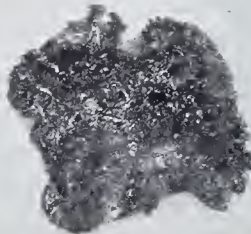


FIG. 2. LUMP SAMPLES OF PITTSBURGH COKING COAL AND SEMI-COKE SUBJECTED TO PARALLEL HEAT TREATMENT

The curves shown in Figure 1 gives results of experiments indicating the relative evolution of volatile matter from coal and from semi-coke at different temperatures. It is evident that the volatile gases are driven out from the coal at lower temperatures and very much more rapidly than from the semi-coke.

Figure 2 is a photograph of small lumps of coking coal and of semi-coke heated under parallel conditions; it shows the swelling and sticking of the pieces of coal and the absence of any such behavior in the coke. This coke is sample C of the table, carrying 14.6 per cent volatile.



FIG. 3. MODERN UNDERFEED STOKER SHOWING FUEL BED

All this data lead simply to the conclusion (which is confirmed by present limited experience) that low-temperature coke, while light and porous, will form a good fuel bed on stoker grates. It will move freely and maintain uniform permeability to the draft, will not swell or stick, will show a combustibility rate (when suitably prepared) greatly exceeding that of ordinary cokes or even of coal, and will require less velocity of air to maintain a given combustion rate.

It will form an even fire bed transmitting radiant heat in high degree to the boiler, producing a very short and entirely smokeless flame. The fusion of the ash in the high temperature zones should

carry down readily (on an underfeed stoker) through the fire, so that clinker will be moved easily to the lower grates and grinders.

With carefully controlled and distributed air supply such as is provided in the modern underfeed stoker of the multiple retort type

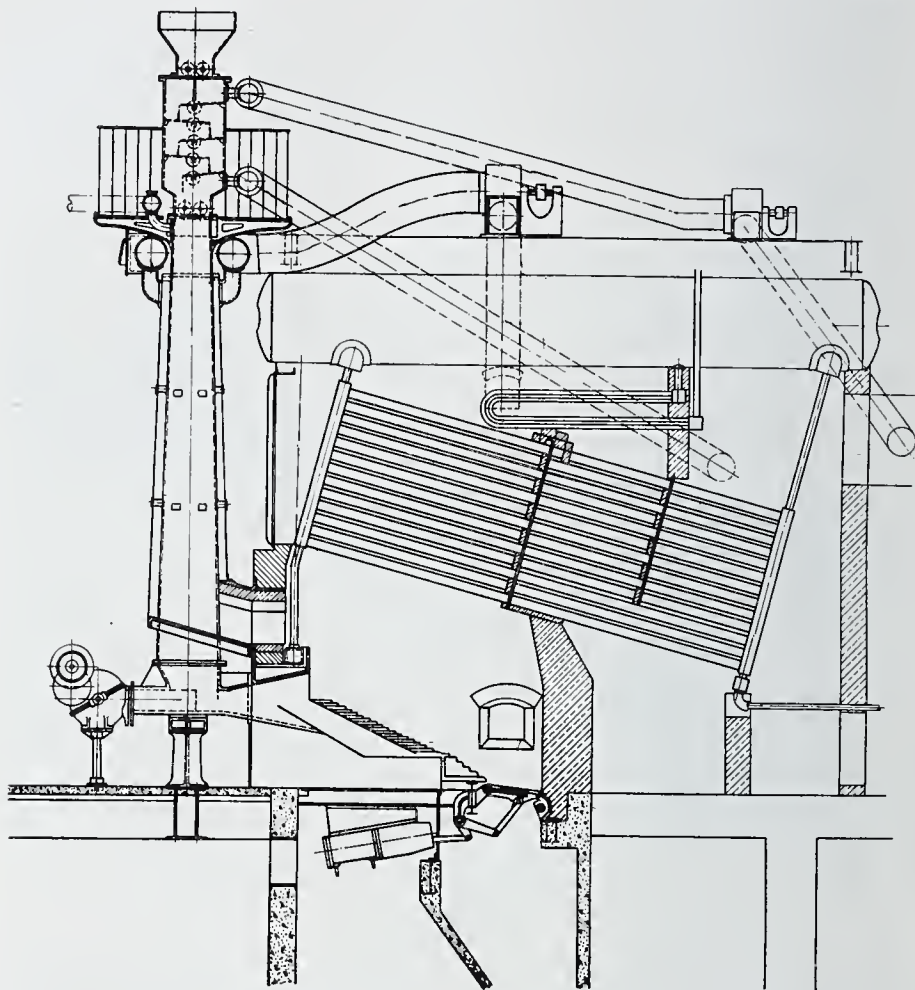


FIG. 4. FUEL TRANSFERRED DIRECTLY FROM RETORT TO BOILER FURNACE FUEL BED

(Fig. 3), a fuel bed of the character just described is capable of very high combustion rates per unit of furnace volume and a steady efficient performance, making for low operating costs.

The use of carbonized fuel thus on stoker grates offers the advantages of a minimum of handling of the fuel, the passing of sensible heat direct from carbonizer to the furnace grates, economy of space, and of structure and machinery.

Within the writer's knowledge, there are four different systems now in operation, either on a small commercial scale or experimentally, in which the fuel is transferred directly from the retorts to some form of stoker, and there is in operation a fifth system in which the fuel is transferred to the form of mechanical stoker, but not directly. Figure 4 will illustrate diagrammatically the manner in which the fuel is transferred directly from the retort to the boiler furnace fuel bed. There are several installations which have been in commercial operation for several years on a small scale, and which the writer has been following with very keen interest.

These systems consist both of the type where the fuel is heated by direct contact with hot vapors or gases, and the type in which the retorts are externally heated by hot gases or vapors. The resulting by-products naturally vary substantially, but the residue fuel or coke is uniform and of a free burning character, and free from smoke making constituents.

It undoubtedly is obvious to those who are familiar with this new art, and I should like to make it clear to those whose interest is just being awakened, that this process is like many others in that its commercial success depends on effecting a variety of small economies. The economics of the situation demand that the investment cost shall be held at the lowest; that the flow of the raw material (fuel) shall be as direct as possible; that its flow shall be interrupted as little as possible; that the recovery of gas and tar shall be simple and direct; that the heating of the fuel must be efficiently accomplished, and preferably with what would be otherwise waste heat as far as possible; that the sensible heat in the fuel (the residue coke is discharged from the retorts at a temperature of 1,000°F.) must be conserved; that the quenching of the hot fuel with water to avoid oxidation of the fuel when exposed to the air represents a very substantial loss, and also rejects one advantage of the system, which is to produce hot fuel, moisture free, and therefore must be avoided.

All of these factors appear to indicate that the fuel should be fired directly after it is discharged from the retort in a suitable furnace and on suitable grates for its burning.

Or, perhaps expressing the matter more briefly, the successful commercial outcome of low temperature carbonization for power station use will go to that system which will have the lowest first cost and also the lowest operating charges.

## BLACK AND WHITE COAL IN AUSTRIA

By DR. B. GRANIGG

*Professor, University of Mining and Metallurgy of Leoben, Austria*

The economic situation of the Republic of Austria, as bounded by the Treaty of St. Germain, was characterized by two essential features. First, the agricultural production did not suffice to ensure an adequate food supply for the population; and, second, the resources of energy heretofore used in the country did not nearly meet the needs for railway, industrial, public and private purposes.

This situation, with regard to the country's supply of energy, led to a very severe economic crisis, which caused a temporary stagnation of the traffic for lack of coal, and partial paralysis of industrial plants, as well as an extreme curtailment of coal for domestic use.

To remedy these conditions the following steps were taken: First, the country's abundant sources of hydraulic power that had not been utilized were rapidly developed in many places. Second, intense attention was directed to the economic consumption of fuel; and the full utilization of the blast-furnace gases and of the waste-heat was effected. High steam-pressure of 30 atmospheres and even of more than 100 atmospheres was introduced in several plants and actually carried out.

In several processes, as for instance the roasting of siderite, new methods were invented with the result that this ore can now be roasted successfully with considerably smaller quantities of even inferior fuel.

Third, the coal mining industry of the country was temporarily enlarged and measures were taken to improve the efficiency of the coal miners. Improvements in coal-washing and dressing rendered possible the full utilization of nearly the whole coal-substance.

Fourth, for all that, the deplorable fact remained, that Austria had no coal fit for the production of metallurgical coke. Besides, the small coal deposits found in the country cannot possibly meet the country's needs. Furthermore, the fact to be taken into consideration, is that the principal bituminous coal deposits of the country were very unfavorably situated for the chief consuming districts.

In order to remedy this, propaganda was employed throughout the country to persuade coal consumers to use, wherever possible, domestic instead of foreign coal.

Some producers of bituminous coal established special industrial consulting offices, where projects for the coal consumers were worked out gratis, with a view to replacing the use of foreign coal by the country's own bituminous coal. A very effective step was the betterment of the quality of inland bituminous coal and consequently the extension of its field of utilization, thus offering a valuable substitute, even in districts where previously only foreign coal could be used.

This aim was attained first by a process of desiccating contrived by Professor Dr. Fleissner. Mention may be made here of the fact that practical tests are being made to improve Dr. Fleissner's process.

For the purpose of this conference I am going to deal with those measures concerning the utilization of hydraulic power and the development of coal mining only in a brief way, whereas ore-roasting and bituminous coal desiccating will be treated more explicitly.

1. The erection of hydraulic power plants. In order to ensure promptly a source of electric energy, and for reasons of obtaining the necessary capital (domestic as well as foreign), which proved to be very difficult, the transversal Alpine valleys were first used for the erection of water-power plants. As a rule these valleys have a great decline, so that high-pressure water-power plants could be erected in a relatively short time at comparatively small cost.

These high-pressure plants offer two more advantages. According to the climate of the country most rivers yield their minimum of water in winter, that is, just in the time of the greatest need of energy, and give their maximum in spring and summer, when the snow and the glaciers are melting, and the need of energy is comparatively small. (Fig. 1).

The form of the surface of these transversal valleys is to a large extent the product of glacial erosion and consists of a succession of flat basins separated from one another by steep chutes. (See Fig. 2.). These hollows can easily be dammed off, to form valuable water-reservoirs, filled up in summer for use in winter.

The longitudinal valleys, which naturally cannot be dammed off on such a large scale, were utilized only to a small degree. The water powers of the river Danube are so far only objects of intense studies and projects. The utilization of water powers was accomplished first by the railway management, which equipped the railway-net from the Bodense and the Swiss frontier as far as Salzburg for electric traction with alternating current of  $16\frac{2}{3}$  cycles. There is good pros-

pect that this electrification of the state railways will soon be extended up to Vienna. Beside the state railway management the provincial governments also promoted the erection of water-plants for public use and industrial purposes, establishing joint stock companies, and taking over the liability for the loans (especially American ones), which were necessary.

On a smaller scale several industries built up water-plants of their own in order to become, as far as possible, independent of coal. It might be mentioned here that more than a thousand smaller hydro-electric plants were erected by the farmers for their own purposes.

The electric network of the various districts has been systematically developed in such a way that most of these plants send their current into the same network, and in the western parts of the republic there is a connection with the Gerasn network.

2. To characterize the economic measures with regard to the consumption of coal it may be said, that particularly in the paper industry steam accumulators after the Ruth system and electric steam boilers for the utilization of surplus of current were amply made use of.

To give an example of economic measures in the iron industry it may be stated that the biggest Austrian iron producing company, which also owns bituminous coal mines, several years ago placed on the market only about 12 per cent of its bituminous coal, and used up the remainder for its own purposes. Today however 46 per cent of the same production of bituminous coal is placed on the market.

This economy in fuel consumption was attained by the complete utilization of blast furnace gases in gas engines and the use of the waste-heat of the Martin-furnaces in waste-heat boilers.

Besides this, the various plants of the above-mentioned company were united by electric lines to assist one another.

3. With regard to the endeavors to meet the full demand for coal out of our own mines, it must be stated that this is a self-evident impossibility. True, Austria possesses, as may be seen on the attached map, some anthracite coal deposits, but these, being geographically unfavorably situated, are so inferior both in quality and quantity, that they are of value only in times of extreme need, as is the case in Switzerland.

The Austrian coal in the Triassic, Jurassic and Cretaceous formations are, as shown in the attached map, more extensive, but generally of varying and little thickness, and their inferior quality justified the erection

of small mines only in a few places. All attempts to enlarge these mines in order to procure a substitute for foreign coals were rendered ineffective by their inferiority in quality and quantity of production. In the same way numerous mines, based on small deposits of bituminous coal of the tertiary formation that had been opened in times of extreme need, had to be closed when it was made possible to get coal from foreign countries.

The endeavors to increase the domestic coal mining is shown by the fact that the output of domestic coal in 1914 was 87,000 tons, whereas in 1927 it amounted to 176,000 tons. This is, however, rather a small production as compared to four and a half million tons of coal imported from foreign countries. The production of bituminous coal in 1913 was 2,600,000 tons, and reached in 1927 3,100,000 tons. But if we take into consideration that Austria also imported about 500,000 tons of foreign bituminous coal, it may be seen that a further increase of domestic coal mining may rightly be expected, presupposed that the consumers will in future use more domestic coal than up to now.

In order to extend the market for domestic bituminous coal and even to replace the imported foreign coal as far as possible by bituminous coal, the above-mentioned measures were taken. The most effective of these measures proved to be Professor Fleissner's coal-desiccating process. In the following I am going to give a brief description of it. Professor Fleissner's process avoids the drawback of crushing the coal in desiccating it. The previously used methods of desiccating bituminous coal by means of hot gases involved the great disadvantage that the drying began from outside, in consequence of which a shrinking of the surface was unavoidable, while the core remained unaltered. The dried surface of the coal used to crack all over until it fell off and this destructive process went on till the whole pieces of coal were crumbled up entirely.

By the Fleissner process the coal is first heated in closed retorts by saturated steam of about 8 atmospheres during one and a half or two hours, whereupon the steam is allowed to escape into another receptacle. Cold or preferably warm air is now blown through the first receptacle containing the coal. Nearly a third of the water is eliminated during the heating of the coal by steam; almost another third of the water escapes during the outlet of the steam, and the last third is gotten rid of by the airing of the coal. The following results as achieved with the bituminous coal of Koflach give the precise percentage of extracted water:

	<i>per cent</i>
During the steaming.....	28.3
During the outlet of steam.....	45.0
During the airing.....	47.7

The technical execution of the process may be seen in the attached sketch. The receptacles are placed behind one another in such a way that the escaping steam is led from one to the other. The first such desiccating establishment erected in Koflach, Austria, works up 750 tons of wet coal within twenty-four hours and the water contents of about 34 per cent is lowered to 16 per cent and the caloric value is raised from 3,400 calories up to 4,700 calories. For the extraction of 1 kgm. of water from the coal 0.65 kgm. of fuel-coal for the steam production is needed.

In this way it was made possible to transport the coal to remoter markets.

During Professor Fleissner's experiments the mining engineers Skutl and Steiner worked out another coal desiccating process, which is just now being put to test. The principal idea of this process is the following: The coal desiccating establishment is identified with a boiler plant, in which the water contained in the coal takes the place of the boiler feed-water. In this way the economy of heat is raised to a maximum. A further feature of this process lies in the coal desiccating by means of higher pressure and superheated steam in such a way that the temperature is gradually increased and that the coal by degrees loses nearly all the water contained in it. After the desiccation of the coal has thus been effected, the coal is further heated to about 300°C. with a view to causing the formation of tar from out of the coal, whereby the pores and fissures in the coal are supposed to be closed when the pressure decreases. According to experiments, bituminous coal with a water content of 28 per cent was desiccated down to a water content of 2 to 4 per cent, and the caloric value of it was raised from 4,300 calories to 6,700 calories. At the same time 250 kgm. of steam of 2 atmospheres could be utilized for industrial purposes per ton of coal. For the desiccation of 1 ton of bituminous coal under the above-mentioned conditions 57 kgm. of fuel coal were necessary. The way this method is carried out is shown in the attached scheme (Fig. 4). In order to start the process of desiccation in receptacle number II saturated steam of 20 atmospheres is conducted from the respective pipes into the receptacle N.-II in order to displace the air therein. Then the small circulation pump  $\bar{U}$  is set to work and as

much superheated steam from the hot steam pipes is added as is necessary to maintain the pressure of 20 atmospheres. This is carried on until the complete heating of the coal has taken place. The further stage is shown in the receptacle III, from which it may be seen that the now saturated steam, which is perpetually forming by the evaporation of the coal moisture, is conducted into the saturated steam pipes and finally into the steam accumulator. During all this time the circulating pump U supplies the heat that is necessary for the evaporation of the coal moisture in the form of a mixture of saturated steam and superheated steam. This pump is regulated by valves. As soon as all the moisture has been evaporated, superheated steam of  $300^{\circ}\text{C}$ . is conducted through the receptacle, as shown in receptacle V, with the purpose of causing the formation of tar during the sudden expansion which takes place when the steam is let out into the open air. For the regulation of the steam circulation there is another circulating pump which is placed between the saturated steam accumulator and the steam superheater.

This process promises a further betterment of coal, yielding at the same time cheap energy.

Another economic measure applying to bituminous coal and concerning the roasting of siderite and such materials has been contrived in Austria. This process has been worked out by the general manager, Dr. Apold, and Professor Fleissner, and works as follows:

Hot combustion-gases are produced in a combustion chamber outside of a roasting furnace which is built in the shape of a shaft-furnace. These gases may have been produced either as blast-furnace gases or gas-producer gases or even such as given by inferior bituminous coal burned on a pluto-stoker. These gases are passed from the combustion-chamber through a series of slits into the roasting shaft. The lower part of the roasting-furnace contains a fit-in saddle to relieve the discharge-table of the weight of the ore-column. Through the lowermost part of the furnace fresh air is forced by a fan which air is heated by the roasted ore sinking down. This heated fresh air causes a further oxidation of the descending ore, its heat being at the same time increased by the oxidizing process. Higher up in the furnace a mixing of the combustion-gases and this heated fresh air takes place. The blowing of a surplus of fresh air through the shaft-furnace brings about a speedy escape of  $\text{CO}_2$  (carbonic acid gas) as formed by the process of roasting, so that the partial pressure of  $\text{CO}_2$  is kept low, whereby the roasting of the siderite takes place at the

relatively low temperature of 650°C. The advantages derived from this process are the following:

1. The formerly necessary consumption of heat of 600,000 to 700,000 calories per ton of ore was reduced to 160,000 to 200,000 calories.
2. As heat resources blast-furnace gas or even inferior coal may freely be used.
3. It prevents a disadvantageous mixing of the ore with the ashes of the fuel coal.
4. The roasting of the ore is executed equally, in consequence of the even flow of hot gases throughout the whole furnace.
5. The daily output of from 10 to 15 tons of charge of old-fashioned furnaces was raised to 200 to 400 tons of those of modern construction, both having the same dimensions; or expressed in other words, the output per cubic meter of effective capacity of the furnace was increased from 0.2-10.3 tons to 6.45-11 tons in 24 hours.

In the above I hope I have shown that Austria's endeavors to utilize effectively her poor resources of coal are not without success.

#### DISCUSSION

CHAIRMAN YOUNG: As I recall it, you referred to Cretaceous and Tertiary coals. May I ask whether the earlier coals are entirely lacking?

DR. GRANIGG: We have in Austria coal of all kinds. For instance, we have graphite. Austria is one of the biggest producers in graphite. Graphite may be shown as clearly as nothing else can. We have near the graphites the same seams and the same layers. You can see the plants of carbonic formation, and in parts of the Alps we have the dynamic changes of transformation of the rocks. You will find coal, anthracite and bituminous, but like Switzerland, these coal seams are sometimes quite ridiculous. They go along several miles and then you find one place where the thickness is from two to four feet, and sometimes more than ten feet, but the thick parts after a few meters, ten to fourteen meters, close again. These carboniferous coals were, as in Switzerland, exploited only during the war, and after the war they were abandoned entirely. They are not in normal condition.

Then we have bituminous coals in the gangu formation, and in the Cretaceous formation. In these formations the bituminous coals at first do not give coke good for metallurgical use. Therefore the coal production is very small. It is a little below 200,000 tons a year. It is much cheaper to buy coal from Czechoslovakia or from Germany.

CHAIRMAN YOUNG: Dr. Granigg, we wish to thank you very much for your courtesy and your splendid paper.

We will now be glad to have Mr. Worker answer questions regarding the paper on carbonized fuel.

DR. GRANIGG: I would be very much interested to know what effect is produced in the United States between white coal and black coal. In Switzerland it is thought that electric traction is much cheaper and more economical than where fuel is used. We had an investigation in Austria within the last few months regarding this. We have very small quantities of coal, but we have plenty of water power, and I should like to know the status of this question in the United States. I know some part of your lines are electrified, but is there no question here of competition between water power and steam power in deciding whether or not to electrify your railways?

CHAIRMAN YOUNG: Will someone kindly answer the question? May I ask if we have some railroad man here whose railroads have been extensively electrified.

MR. ROBINSON: I can tell you what the trend is here. It is more or less of an economic situation. The trend is toward the electrification of our transportation in those communities where it will possibly pay. The investment cost I imagine is very high, and I think that controls the situation rather than the fuel investment cost. For instance, we have now between Philadelphia and New York the electrification of those transportation systems (that is, our largest ones) and they will probably be electrified from New York, past Philadelphia, to Wilmington. We also have an electrified road in the West. You probably know of that one.

I do not think that fuel here is an element of much consideration, because we are commencing to build central power stations to take care of the current that is required for this electrification. Although I have never gone through any of those studies, I imagine it is a study of economics in connection with the making of current in central stations and delivering it to the transportation companies.

A. H. BABCOCK (Southern Pacific Company, San Francisco, Cal.): Answering Dr. Granigg's question directly, I may say that I have studied this very subject for nearly thirty years in connection with one of the largest trans-continental railroad systems. I therefore feel qualified to speak in regard to that property. I would not want my remarks to be taken as a criticism of any of the eastern projects. It is not a question, Sir, of competition between hydroelectric power and steam power in any sense, for the reason that in the West the time of maximum transportation demand is at the time of minimum water. In September and October we have our largest freight movements. We have no rain in the West from April until October. Consequently, all of the large transmission companies in the West are obliged to have steam. About one-third of the plant is in steam.

Furthermore, as a purely economic question we have found that the price of hydroelectric energy per kilowatt hour is fixed by the price of fuel. That, I think, is a general statement that is entirely correct. Therefore, whether a railroad electrifies its lines does not depend in any sense on the cost of power but entirely on the question of whether in the end it can haul the freight for less money, all things included, by steam or by electricity, or if you have

reached the limit of track capacity, steam will no longer haul the loads over the line economically, because if you put electric tracks in you can haul larger loads at higher speeds.

Another point that comes up is the terminal section such as they have in New York and as we have had in the suburban lines on San Francisco Bay, where the public demand for higher speed, cleaner service, forced an electrification of suburban lines long before it was profitable. Those lines were put in operation in May, 1911, and never yet have gotten off the wrong side of the balance sheet.

Then we have in this country tunnel situations where it is practically impossible to haul the loads that are given to the railroads through those tunnels by steam. In other words, it is not so much as yet a question of economics in the cost of power at all in any sense, but it is a very large question as regards the economic operation of the railroad as a whole.

CHAIRMAN YOUNG: Are there any questions directed particularly at the burning of carbonized fuel? In the street cars of Pittsburgh I believe we are using a form of carbonized fuel for heating the cars. I think I have seen that in a number of cities. I am wondering whether or not that is as general as it appears to be, and if so what the next step is going to be in the way of heating cars. Apparently, the heating of street cars by electricity is more expensive than heating with coke. Do you care to make a remark on that, Mr. Worker?

MR. WORKER: I do not know anything about that.

CHAIRMAN YOUNG: Are any of the railroads using carbonized fuel in the sense which we have discussed here this afternoon for fuel in locomotives?

Coming to the general topic of locomotive fuel, I have the names of a good many railroad men here and I am wondering whether Mr. Daly of the Northern Pacific Railway is here. Mr. Daly, do you care to make any comments on the paper?

M. A. DALY (Northern Pacific Railway, St. Paul, Minn.): The first impulse that comes to me in an opportunity like this, commenting on Mr. Robinson's paper, is to say what I think about it, that is, it is very thoroughly done. The ground which Mr. Robinson happened to cover in that paper was tremendous, and no one realized it probably more than he did, for he has made a special study of the developments and of the possibilities, past, present and future, in the utilization of fuels on locomotives.

I admired the neat way in which he put together all of these things. I suppose I ought to stop right there, but your Chairman as I came along said in view of the fact that a number of the railroads in the West were outside of the bituminous field proper, I thought they were improperly out of this conference to some extent, but it seems not. Those railroads are particularly interested in developing for locomotive use the lignite deposits that lie adjacent to their lines, if not directly on those lines. Of course, that is true, and I think in a general way very little can be said as to what extent that development may lead us to. One of the railroads in the Northwest, however,

is at the present time using about a million tons of lignite coal on locomotives, the coal being a black lignite having a B.t.u. content of approximately 8,400 B.t.u.

Some of the railroads in the Southwest are utilizing lignite coal of even lesser B.t.u. A few years ago we used to think—in fact, I know it was a matter of common statement—that lignite coal having a high moisture content of 25 or 35 per cent moisture, could not be used successfully on locomotives of the present type or construction of firebox. We have learned in the experiments that have been made on some of these railroads in the last few years, a number of things that have allowed us to readjust our prejudices against those coals. For instance, the lignite coal can be used—coal of 8,500 B.t.u. is actually used in very exacting service in main line passenger locomotives, and strange to say instead of that coal being regarded as we usually regard a coal of lesser B.t.u., as an inferior coal for the successful service of a locomotive, it is just the opposite. Crews in becoming familiar with that coal prefer it to the better coals which it has succeeded.

There are other favorable characteristics about the utilization of that coal. I think I can speak freely in that way, and almost enthusiastically, about lignite even among my bituminous friends, because the lignite of the West is clear outside of the field of the bituminous districts. I do not know of any bituminous field that would be seriously affected by the development of the lignite, because as far as the Northern Pacific Railway is concerned, we could not afford to haul bituminous coal into the districts where we are now using lignite.

I mentioned that favorable characteristic. It is an odd thing and it will be a striking thing in view of some of the papers that were read this morning at another hall in which the clinkering and ash content, taking care of the ash content of coal, was discussed. The lignite coal having something less than 1,900 B.t.u. offers practically no clinkering problem in their use on these locomotives of the Northwest. Why? The rule ought to be just in the opposite direction. Because apparently, there is a congealing effect, or a hardening of the ash content in the lignite coal, so that it becomes porous and dribble and easy to handle, and we have trains running 300 miles without cleaning the fire, without even shaking the grates at times.

Those are facts, of course, which are merely at the present time coming to mind. They are things we might say we are learning. It is a fact that on our own road we have a staff that is doing nothing else but trying to find out what they can about the lignite coal to utilize it more effectively. A number of other railroads in the West are studying it also. No doubt it has a place in the bituminous coal conference.

If there is anything about those remarks which you may utilize in the study of the development of fuels on locomotives, it will be decidedly interesting to many of the railroads which are within the next few years likely to take up lignite coal in their respective districts in locomotive service.

CHAIRMAN YOUNG: Is Mr. J. M. Nicholson of the Santa Fé System here? If he is I would like very much to have him come forward.

J. M. NICHOLSON (Santa Fé Railroad, Topeka, Kans.): Fuel problems with railroads differ materially. I am connected with a western railroad and our problem primarily is that of getting the most economical fuel from the sources of supply, which are widely scattered over our territory. Our road is one burning fuel oil over 60 or 65 per cent of its total fuel requirements. We are located in territory of the Mid-Continent, Texas and California oil fields and secure some oil from the Tampico, Mexico fields.

Our coal varies from 13,000 B.t.u. to 7,500 B.t.u. in lignite territory. We have a problem of considerable moment in districting this fuel so that the locomotives on the territory will be drafted to burn the fuel furnished. On our road last year the cost of fuel averaged between \$12,000 and \$13,000 per locomotive, and in that assignment we have a number of locomotives with fuel consumption for the year, which averaged \$33,000. That is greater than the cost of repairs on the average locomotive.

I know that the railroads are more than casually interested in the developments and results secured from research on bituminous coal. We are told that we will have to eventually give up our fuel oil, and when the cost becomes prohibitive, we will have to go back to coal.

The problem of the economical use of coal is being studied. Locomotives are being improved from time to time in the way of front end, grate and ash pan arrangements, for no other reason than to burn the fuel more economically. Considerable study is given this subject and work is being done in a constructive way. It is going to mean we will get more efficiency out of the fuel used.

CHAIRMAN YOUNG: Is Mr. Crawford of the Standard Stoker Company here? I would like to hear from Mr. Crawford.

D. F. CRAWFORD (Consulting Engineer, Pittsburgh, Pa.): All railroad men are interested in the fuel problem because of each dollar received by the railroads an amount of six to eight cents is spent for fuel as an average over the United States. Of course, it is a greater sum where the freight charges on fuel, due to their remoteness from the mines, causes a greater expenditure.

Many devices have been invented and applied to locomotives, but, as a matter of fact, the entire subject of locomotive fuel is subordinated to getting the train over the road, as Mr. Robinson has referred to. This puts a very severe handicap on the fuel department because the thought is not to save fuel but to produce transportation.

The stoker has been referred to. I have had some familiarity with the development of the locomotive stoker, and it will probably be interesting to know that perhaps 50 per cent of all the fuel used by the railroads today is used in stoker-fired locomotives. There are between 12,000 and 13,000 locomotives equipped with stokers at the present time.

The problem of stoker coal, coal suitable for stokers, which Mr. Robinson referred to, is, of course, an important one to the railroads. Not only the tests made by the railroads, but by the various universities where locomotive testing plants were available, and they confirm the figures which Mr. Robinson has given you regarding the effect of fine coal. I believe also that the testing plant of the Pennsylvania Railroad, located at Altoona, has shown similar results.

CHAIRMAN YOUNG: I would like to call on my good friend, Mr. Collett, of the Frisco Company, for a few remarks. I realize some of the railroads have a big job in taking coal from very many different seams and different localities. Mr. Collett has had some experience along that line.

ROBERT COLLETT (Frisco Lines, St. Louis, Mo.): I think the greatest message that the railroads can give to the conference is that we are getting to the point now where we can serve you best and help you best by using whatever kind of fuel you gentlemen in the research departments can find for us to use. That applies to the gentlemen of the coal industry, too. I understand, by the way, that the primary conception of this conference was to help the coal industry.

As Mr. Robinson and the other gentlemen very aptly stated, the railroads are using less coal all the time instead of more. It takes about half the amount of fuel to haul a unit of freight one mile of what it took ten years ago. We used to waste a great deal of coal, so it may be fairly expected we are not going to be able to help you a good deal by using a larger amount of coal. We can help you by using the kind of coal and the kind of fuel that is most profitable to the industry generally for us to use.

On the road that I have the pleasure of representing, the Midwestern road of the Frisco Lines, we use about 5,000 tons per hundred cars of coal per day, in round numbers, and about 3,000 barrels, or 30 carloads of fuel oil per day. As your Chairman has told you, this coal comes from several different fields, six fields principally. From all but two of those fields we use resultant coal. In other words, the operator sells the commercial product and we use the other. The railroads can burn slack if you want them to, but it is not commercially practicable generally that they do so.

Due to the good offices of Mr. Crawford and similar gentlemen, they have provided mechanical stokers and modern engines that are capable of utilizing whatever is best for us to do. We do not use oil altogether because it is cheaper, but because, as it concerns our own road, the petroleum industry furnishes 15 per cent of the commercial traffic, the bituminous coal industry about 25 per cent, which is a total of about 40 per cent. That is one thing for the railroad folks to take home with them, that we are primarily standing by ready to serve.

CHAIRMAN YOUNG: Does anybody have any specific question he would like to have answered on any of these papers?

E. L. LANNERT: (Deputy Smoke Commissioner, Cleveland, Ohio): I would like to get some information about the sprinkler type of stokers. They seem to be used in locomotives but are not used so much in stationary plants. I would like to know why they are used so much in locomotives and whether there is a possibility they may be used at some time in stationary plants or in marine plants.

MR. WORKER: Probably Mr. Crawford could answer this stoker proposition better. I will answer you quite briefly. The reason for the stoker on the locomotive is on account of the saving of labor. I think there are sprinkler-type

stokers. They are not generally used but I think the name of one is the Simplex. These stokers throw the coal in over the fuel bed.

MR. LANNERT: I heard of them being used in England, but evidently they are not popular. I guess they are almost universal on the stoker fire locomotives, are they not?

MR. WORKER: The reason they are not used generally is due to this fact: Some are automatic and throw the coal in mechanically instead of a fireman throwing it in, that is, as far as stationary work is concerned. They do not move the ash to the rear of the furnace nor do they do any of those automatic things that a stoker should do.

MR. LANNERT: What are the limitations of the fusion point of ash? Can you use any type of coal or do you have to use a coal with a high fusion point of ash?

MR. WORKER: Because of the very nature of the diffusion where you throw green coal possibly over an incandescent fuel bed, if you had a low temperature fusion of ash all you would have would be clinker, because the fuel bed does not move and it would clinker up on top of the other.

MR. LANNERT: Maybe that is why it is not very generally used, because I remember reading about that device about fifteen years ago. I have not seen any recent installations of that at all.

CHAIRMAN YOUNG: Mr. Crawford, can you make any remarks on these questions?

D. F. CRAWFORD: I will be very glad to answer the question. All of the stokers in the locomotive service at the present time are of a type that feed the coal above the fire. This is brought about almost entirely by the limitations imposed by construction of the locomotives. The coal is carried forward by a screw conveyor and is then raised by some form of elevator, or is pushed up by the initial conveyance screw and deposited on a firing plate bearing some relation to the surface of the grate. From that the coal is either injected by steam or as in some stokers by moving vanes, which sweep the coal off the firing plate.

Underfeed stokers were applied to some locomotives a number of years ago, several hundred of them, and were removed on account of the fact that the maintenance expense due to the intense fire, burned out the conveyor trough. The stokers worked successfully but were quite expensive to maintain. I do not know of any stoker at the present time, of the 12,000 stokers in service, that are not what the gentleman has described as the sprinkler type, which we generally refer to as the overfeed type. Does that answer the question?

As to the ash, I regret that I cannot give any definite information because, as Mr. Robinson stated, all types of coal are being used with stokers, and the results obtained with the very large number in service are such that they do

not regard the formation of clinkers with average coal as serious, or I have not heard of it being so regarded.

H. C. PORTER (Consulting Engineer, Philadelphia, Pa.): I am particularly interested in the subject of Mr. Alpern's paper presented by Mr. Worker. I wonder if Mr. Worker could tell us in a few words how such plants as he has described are operating abroad? I have talked over these matters a little with Mr. Alpern and I know that he has visited such plants using pre-carbonized fuel abroad. I would like to hear how this type of fuel operates on stokers that are actually using it.

A paper was presented this afternoon in another section by W. H. Allen, of the American Gas and Electric Company, on the low temperature of carbonization of coal in an experimental plant at Puilo Station, Ohio. This company is a power company. Their plan is to prepare carbonized fuel, not in an attached retort on the stoker of the furnace, but in a separate unit; then to screen the product, and sell at relatively high prices the larger coke to the domestic trade and use the smaller sized fuel on chain grate stokers under their boilers.

Mr. Allen tells me the results have been favorable. Just as Mr. Alpern in his paper indicated as probable this pre-carbonized fuel maintains a physical condition on the stoker that is desirable since it seems to give less "fly-ash" under high capacities, and less trouble with blowing of the fuel out of the furnace chamber.

This morning Mr. A. R. Smith, of the General Electric Company, in his survey of the future of power production alluded to the possibility of carbonizing or processing coal, and to the scheme of carbonizing coal in a separate plant, and having the operations in two separate units, and said it had not so far proved economical.

The scheme Mr. Alpern outlines, and which has been tried out abroad, of having a direct connection between the carbonizing apparatus and the stoker grate, seems to show more promise, giving the great advantage that he has mentioned of cutting down fixed charges and unit plant cost.

MR. WORKER: Regarding the question as to whether I have any information on these foreign plants referred to, I wish to say I have no detailed information. Mr. Alpern mentioned in the paper he had visited four plants abroad that are more or less working out this process where the residue coke is transferred directly to a grate. One plant in particular, I understand, is working very satisfactorily. That is where they have the retort in front and the coke is delivered onto a chain grate type of stoker.

To my mind there are two differences in Mr. Alpern's ideas and those abroad, and that is he gets from an investigation of these plants that they hardly pay, that is, the process itself, and these processes abroad were designed toward taking out the by-products and making it pay. So he has brought up this new idea, that even if the process does not pay, considering the high cost of our stations today, power stations, we are going to more than make that up in the reduction of the fixed charges, probably the operating expense and those elements of the process.

# PRESSURE ELECTROLYSIS—POWER AND FUEL

## OXYHYDROGEN IN THE INTERNAL COMBUSTION MOTOR

By J. E. NOEGGERATH, DR. ING.

*Berlin*

Everyone knows that it is the tendency of modern engineering, of modern economics, to concentrate power into small space, to make machines and apparatus as compact and simple as possible.

It is therefore not to be wondered at that during the past thirty years many inventors concentrated their efforts to the problem of producing, electrolytically, in pressure cells, hydrogen and oxygen at high pressure directly, i.e., without using compressors.

Aside from the desire to eliminate the compressor, its space and first cost, labor and operating cost connected therewith, inventors were stimulated by their experience, first recognized by Hausmeister and Professor Cöhn both of Germany, that electrolysis at high pressure requires less power than at atmospheric pressure.

This surprising fact does not infringe upon the law of physics.

These early investigators neither recognized the integrate sum of causes producing this astounding phenomenon nor the fact that it holds good only under certain conditions. So all attempts to build an efficient and practical high pressure cell failed. In a paper I read before the German Engineering Societies at the Technical University of Berlin-Charlottenburg on December 14, 1927, (fully reprinted in the *Zeitschrift des Vereins Deutscher Ingenieure*, 1928 No. 11, and partly reprinted in the July number of *Chemical and Metallurgical Engineering*), I developed the theory of pressure electrolysis and the reasons for the change of electric energy required as the pressure of the gas is varied. This subject will therefore be touched upon lightly in the course of this paper.

As a matter of fact the energy required to generate hydrogen and oxygen by electrolysis does not necessarily drop with the increasing gas pressure, but may drop, rise or fall, according to the inherent qualities of each cell type.

Now before describing these electrolytic plants and giving the results of the tests made by the Technical University of Charlottenburg and the German State Railways I shall speak of some of the applications and their relation to power and fuel.

In considering the economic value of producing pure gases by pressure electrolysis, that is in a cell where the gases and the pressure are generated simultaneously without the aid of compressors, it is, of course, possible to calculate for each separate one of the usual applications, what saving and other advantages can be derived by considering the cost of power, the first cost, the saving in space and in labor. But beyond that, the general economic situation of a power plant may be much more favorably affected than would appear from such calculations; it has to be considered that the hydrogen is produced with a very high degree of purity and, that, as with atmospheric electrolyzers it contains only oxygen, and no other impurities.

For these two reasons, in the purification plants the catalyzers are reduced in size and may wholly be eliminated in many cases; this saving in capital cost and labor cost has to be put to the credit side of pressure electrolysis.

From the list of applications given below and considering all the items of cost it will be found in many cases that the pressure cell guarantees a method of gas production superior to the methods hitherto known.

But beyond that this method would in many cases prove successful in reducing in many power stations the cost per kilowatt hour. For instance, the current at the period of off-load may be used for pressure electrolysis: if the power station is large enough synthetic ammonia may be so produced or oils from coal and so forth. The capital service per kilowatt hour for the normal phase of the power service may so be considerably reduced.

Or, under favorable conditions the current used for the production of hydrogen and oxygen may be calculated in at practically nothing without affecting the rentability of the power plant. The new pressure cell, therefore, not only offers a method of using the surplus current in connection with a vast number of applications but also a method to cheapen expensive kilowatt hours.

The applications of the pressure electrolyzer may be divided into two groups.

Group I covers the processes where no mechanical energy is gained directly.

Group II the processes where mechanical energy is gained by the use of hydrogen and oxygen.

Among the first group of applications there may be mentioned:

1. The production of hydrogen for the manufacture of synthetic ammonia.

2. The production of hydrogenation of coal and oils.

3. The improvement of long distance gas transmission, particularly in view of the fact that in the pressure cell the pressure not only costs nothing but reduces the cost of production.

4. The use of oxygen or oxygen and hydrogen for welding and cutting.

For these and other purposes, especially for comparatively small quantities the gases were so far usually sold in pressure bottles.

Now, however, it will frequently be advantageous to sell pressure cells instead of the gas.

The type of high pressure cell used for this purpose has the shape of a large gas bottle. In fact, it is simply a normal high pressure bottle containing the electrodes, etc.

They of course, do not require compressors; they are self contained and each cell is operated at 110 or 220 volts.

The customer no longer bears the transportation of the gas in bottles nor the delay and inconvenience that may be connected therewith. In short, even for the small consumer the gas production is decentralized.

Continuing with the second group of applications:

5. In some countries the production of high grade glass is done with hydrogen.

6. The manufacture of margarine.

7. The manufacture of soap.

8. Storing of energy. It frequently does not pay to electrify the branch lines of electrified trunk lines. But it does pay to use their cheap off-load current to produce hydrogen out of water electrolytically to run the branch line trains with. A romantic German friend of mine calls this "making fuel out of water," as these cells form the part of a water power plant he might have said, "making fuel out of water with water." I prefer to call it indirect electrification.

Of course, ordinarily it will not pay to make this detour, to transform electric energy into the heat energy of hydrogen for the purpose of obtaining mechanical energy, but when you transform, as you do in this case, not only the energy but also its money value by making use of the off-load, a sound proposition presents itself.

The above applications may frequently serve for improving a

given power plant situation in an indirect way, so to speak. The second group of applications however, is capable of improving fuel, power directly.

Professor Buschmann, an authority in the German automobile industry, made the brake tests shown in Figure 6. In a stationary gasoline motor oxyhydrogen was fed to the fuel.

The curves on the left show how the output of the ordinary gasoline motor was increased by the addition of the gases and how the fuel consumption was considerably diminished.

The curves on the right show how it was possible to operate this gasoline engine with a heavy oil (Solar-oil) at a fuel consumption equivalent to the reduced fuel consumption of the gasoline.

The first equipments of this kind were proposed by French engineers whose names I unfortunately could not learn and by Hausmeister, one of the pioneers of the pressure cell and in this field of cell application. But while the efforts of these men indicated the way they did not fully succeed; for only a stationary motor, not a motor car, could be operated with this equipment, nor could very heavy oils be used, nor the stationary motor started without additional starting means.

Now, however, this problem is solved by the aid of the oxygen hydrogen cell electrically coupled to the motor plant and the latest development of my cell-motor equipment enables me to say that the motor-bus, truck, motorboat and the aeroplane burning in its normal gasoline motor oil instead of gasoline or benzol is well under way.

As the patents are not issued I am unfortunately not permitted to disclose publicly the details of these processes. But I can say this much: the motor drives a small lighting dynamo. Its current produces in a very small cell a certain amount of hydrogen and oxygen and these gases are added to the fuel. They are ignited first, acting much like a detonating fuse permeating a charge of explosives. The small local explosions of the gases tear the oil drops into tiny fragments of infinitely large surface. Besides, as less air is used for combustion, less heat is carried off by nitrogen.

As a result the motor requires less fuel though it has to drive the very inefficient small dynamo and thereby the cell. These motors can so be operated both on gasoline and oil with a reduced fuel consumption. So if the price of oil should in time rise to a prohibitive figure and until oil can be had everywhere, gasoline may be used.

This development is applicable to other processes of combustion.

There is reason to believe that boilers operating with pulverized coal and the efficiency of small Diesel engines may be improved.

Now let me describe in short how the electrolyzers are built for these various applications, how they work and what results were obtained.

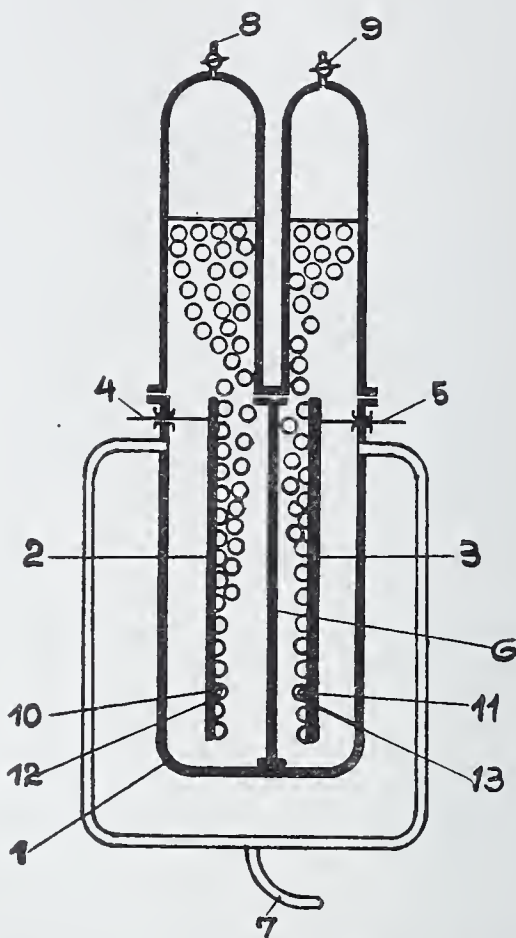


FIG. 1. DIAGRAMMATIC SKETCH OF PRESSURE ELECTROLYSIS

Figure 1 represents diagrammatically a pressure electrolyzer. In the vessel shown electrodes 2 and 3 are inserted to which the current is supplied at 4 and 5. The gases are kept separate by the diaphragm.

When the current is supplied, with the valves 8 and 9 opened, hydrogen and oxygen gas bubbles (10 and 11) are generated; they rise into the containers situated above.

When the valves 8 and 9 are closed the gas production continues and as more and more gas is generated the pressure in the gas spaces (below 8 and 9) increases. It can be increased up to the pressure at which the specific weight of the gases equals that of water, i.e., to about 1800 atmospheres. If the temperature is low, that is if the oxygen liquefies, then the pressure up to which the pressure electrolysis can be brought up is reached when the specific weight of the hydrogen equals that of water.

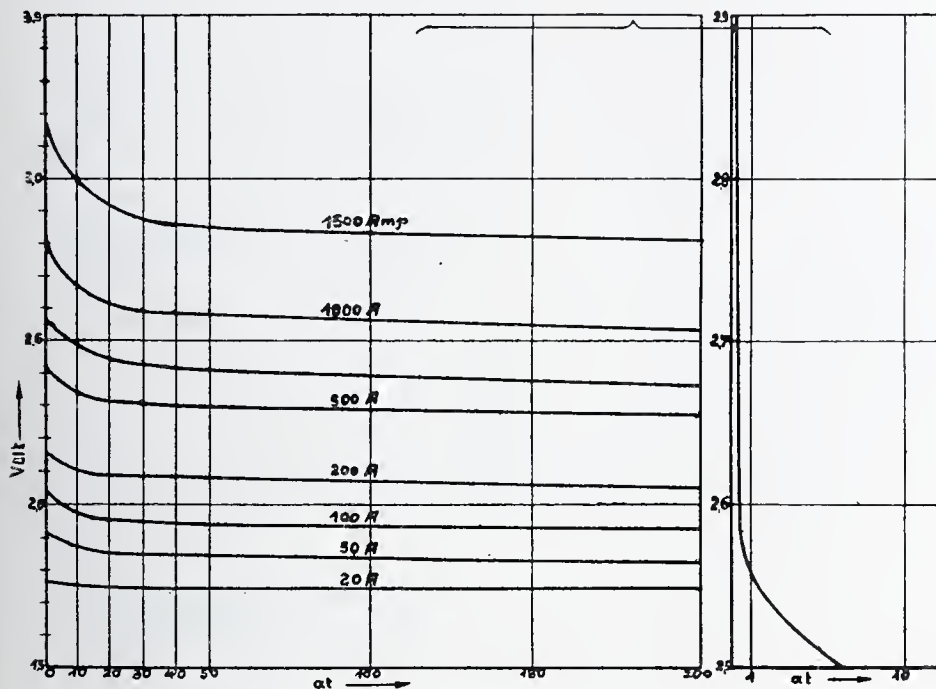


FIG. 2. DROP IN VOLTAGE WITH RISING PRESSURE AT VARIOUS AMPERAGES IN ELECTROLYZER

*Left:* Above atmospheric pressure. *Right:* Below atmospheric pressures

As with ordinary water electrolysis, i.e., with atmospheric electrolysis, hydrogen and oxygen are produced in the ratio of 2:1 and if the separation of the gases is perfect the quantity of the gas produced follows Faraday's Law. If, however, a considerable mixing of the gases takes place, e.g., if no diaphragm or imperfect diaphragms are used, a part of the gases combines in the electrolyte to form water and the useful gas output is reduced.

The left part of Figure 2 shows the relation of voltage to the current at various gas pressures and temperatures of the electrolyte, the voltage

being the deciding component for the measurement of the specific energy, namely the energy required to produce 1 cubic meter of gas (measured at atmospheric pressure (760 mm.) at a gas temperature of 20°C., but compressed at the gas pressure indicated).

The drop in voltage with a pressure rise from 1 to 200 atmospheres is clearly seen. On the right hand side of Figure 2 the even more surprising drop in voltage that occurs with rising pressure, but below atmospheric pressure becomes evident.

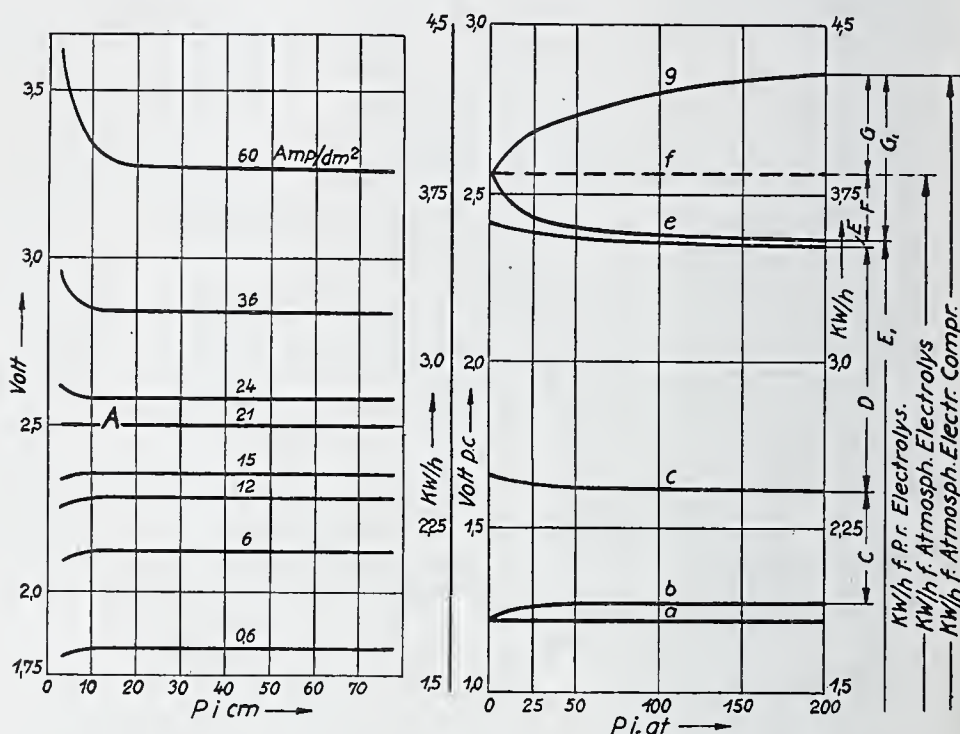


FIG. 3

*Left:* Drop or rise in voltage with rising gas pressure in the full range of amperages of the electrolyzer. *Right:* Influence of gas pressure on the various components of voltage and of specific energy.

As was said at the beginning of this paper the voltage does not necessarily decrease with increasing gas-pressure but may be constant or rise.

This is clearly seen in Figure 3 (to the left) where the upper curves show a decrease of voltage with increasing gas pressure while the middle curve A, the "critical" voltage (at a "critical" amperage) remains constant and the lower curves show a tendency to rise.

I was fortunate in being able to announce and to prove, in my Berlin lecture, the following new laws of electrolysis:

1. With rising gas pressure the voltage and specific energy consumption remains constant, increases or decreases according to the specific volume of the gas produced.

2. With a definite critical voltage, and current density—characteristic for a given cell type—the current density and the specific energy consumption remain constant at all gas pressures.

3. In approaching “infinitely high” pressure the voltages at all current densities approach the critical voltage.

4. In approaching “infinitely low” pressure the following holds: Above the critical current density the voltage required to electrolyze approaches the infinite, i.e., electrolysis tends to become impossible. At the critical current density, the critical voltage is required. Below the critical current density the voltage drops, evidently tends to approach the theoretical value of 1.23 volts. The type of pressure electrolyzers which is designed for voltages and specific energy consumptions that decrease with increasing voltage are at present those best adapted for commercial use. How their various components are affected with decreasing gas pressure is shown in Figure 3 (right hand side).

*a* is the theoretical voltage (1.23 volts) required to split up the water. *b* is the small surplus energy required to electrolyze with increasing pressure.

*C* shows the slight decrease in voltage due to the decrease of polarization: The gas bubbles on the surface are reduced in size due to the pressure whereby the resistance in the path of the current is reduced.

*D* shows the slight decrease of the pure ohmic resistance of the electrolyte on account of the pressure affecting the degree of dissociation.

*E* and *e* finally show how the gas pressure reduces the volume of the gas bubbles rising in the electrolyte. This reduction of the size of the gas bubbles means that the free section of the electrolyte becomes larger at high pressure than at low pressure and the path traversed by the electrons a more direct one. Thereby the apparent ohmic resistance is decreased.

It is evident from Figure 3 that the components of voltage reduced by increasing pressure dominate over those that are increased; as a result the total voltage and specific energy consumption is measurably reduced:

*f* shows the voltage and energy consumption at atmospheric pressure.

*g* shows these values at atmospheric pressure plus the energy consumption required by mechanical compressors and their drive, while

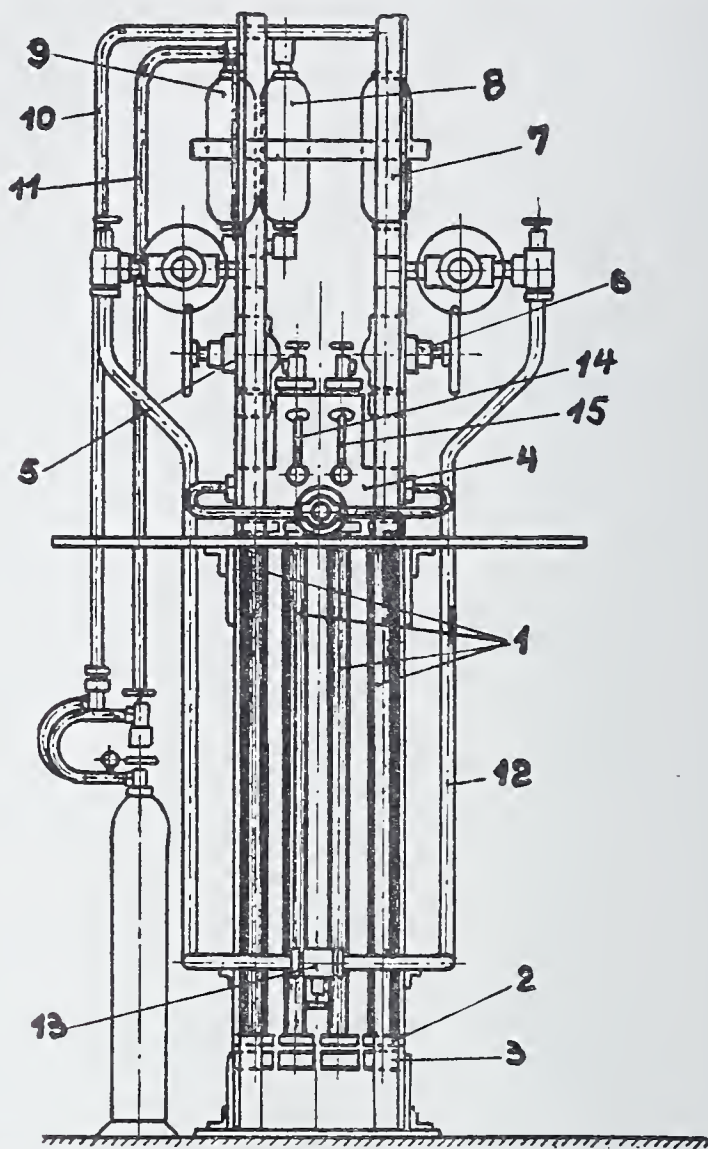


FIG. 4. NOEGGERATH PRESSURE CELL FOR 150 ATMOSPHERES

*e* shows the much lower energy consumption that is required if the gases are produced by pressure-electrolysis.

*G1* represents the corresponding gain in voltage and specific

energy. Its value may vary in accordance with the left hand side of Figure 3.

Figure 4 represents a pressure electrolyzer for 150 atmospheres which has been in operation for about two years and is in operation now. It is built up of a number of steel pressure tubes which form the walls of the pressure cells. At the same time these tubes form the outer electrodes. They surround the electrodes of the opposite polarity within from which they are separated by a concentric diaphragm tube.

The current is admitted at 2, it passes to the outer electrodes, then through the electrolyte, and the diaphragm tube to the negative electrode within, thereby generating hydrogen and oxygen, in an almost perfectly unmixed state. The current leaves the cell at 3.

In the forged block 4 the oxygen and hydrogen is separately collected from the various cells. The hydrogen passes through the electrolyte vessels 8 and 9, the oxygen through the vessel 9 to the respective gas bottles. At 13 the water is supplied to the cells under pressure.

Figure 5 shows the design for a pressure electrolyzer which is being built for the German State Railways. Here the individual cells are inclosed inside of a pressure vessel. The plant is designed for an output of 60 cubic meters an hour, or about 15 million cubic feet a year. The floor space is only 2 square meters.

The design represents a medium size plant for railway welding work. At the same time it is the unit from which large plants for ammonia production, hydrogenation, etc., are to be composed. The first plant was thoroughly tested and under constant supervision by the Berlin Technical University and the German State Railways, and the figures given for specific energy consumption, purity of gas, safety of operation, etc., are taken from these tests.

The results were:

1. According to the load the specific energy consumption varies from 3 to 3.5 kilowatt hours, per atmospheric cubic meter of gas, compressed.
2. According to the operating conditions the purity of the gas varied from 99.1 per cent for oxygen to 99.9 per cent for hydrogen; under certain conditions the average gas purity was higher than 99.5 per cent.
3. The pressure control was perfect. In several tests a hydraulic pressure of up to 300 atmospheres was gradually supplied to one

gas side of the apparatus, but the manometers of both sides always showed equal pressure.

4. The operation proved to be absolutely safe and the danger connected with hydrogen and oxygen compressors was completely lacking.

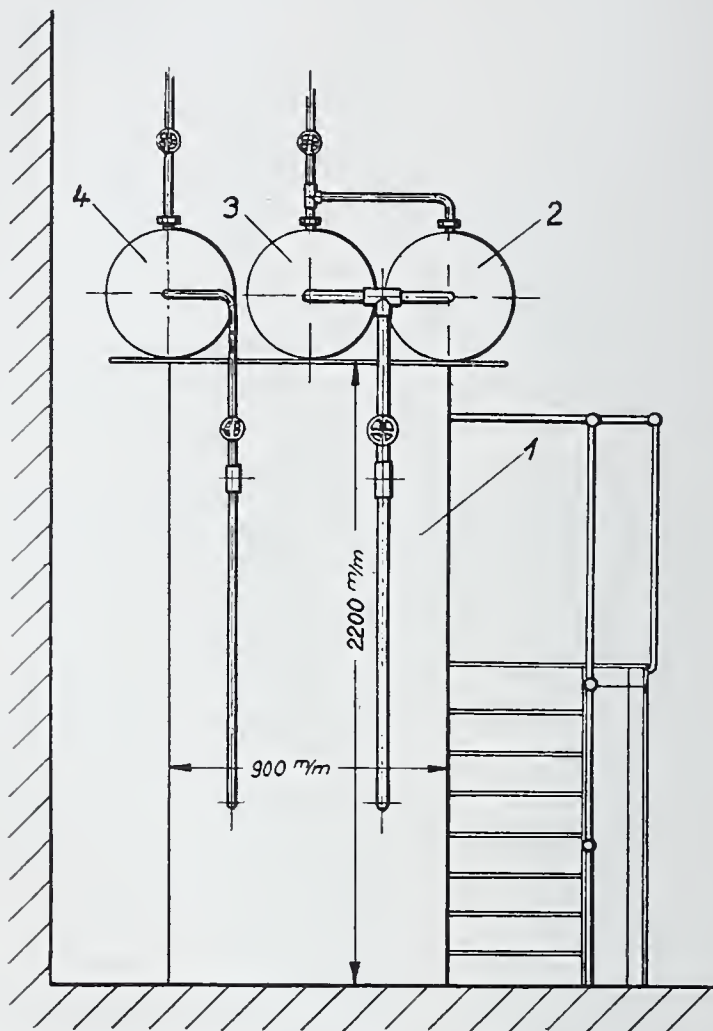


FIG. 5. NOEGGERATH PRESSURE CELL PLANT FOR GERMAN STATE RAILWAYS  
110/220 VOLTS 200 ATMOSPHERIC 60 CBM./H.

The laboratory experiments of Hausmeister up to 380 atmospheres and Professor Cöhn up to 3000 atmospheres with small quantities of gas showed that the electrolytic compression of the fully mixed gases (oxyhydrogen) is perfectly safe. The reasons for this high degree of

safety are given in detail in my paper mentioned above. I compressed even the gas mixture, the oxyhydrogen in commercial quantities, up to 150 atmospheres without any detrimental effect.

5. The size of the plant is much smaller than those of atmospheric electrolyzers, even not counting their compressors. The floor space is one-seventieth of the older atmospheric designs, one-tenth of modern atmospheric cells and frequently much less.

N.S.U. Motor No. 5375    --- with Dynamo running light    --- Solar-Oil with  $H_2+O$  fed to Motor  
 Diam 66 mm    --- with Dynamo feeding cell    --- Benzol with  $H_2+O$  fed to Motor  
 Stroke 90 mm    --- with Dynamo feeding cell and  $H_2+O$  fed to Motor

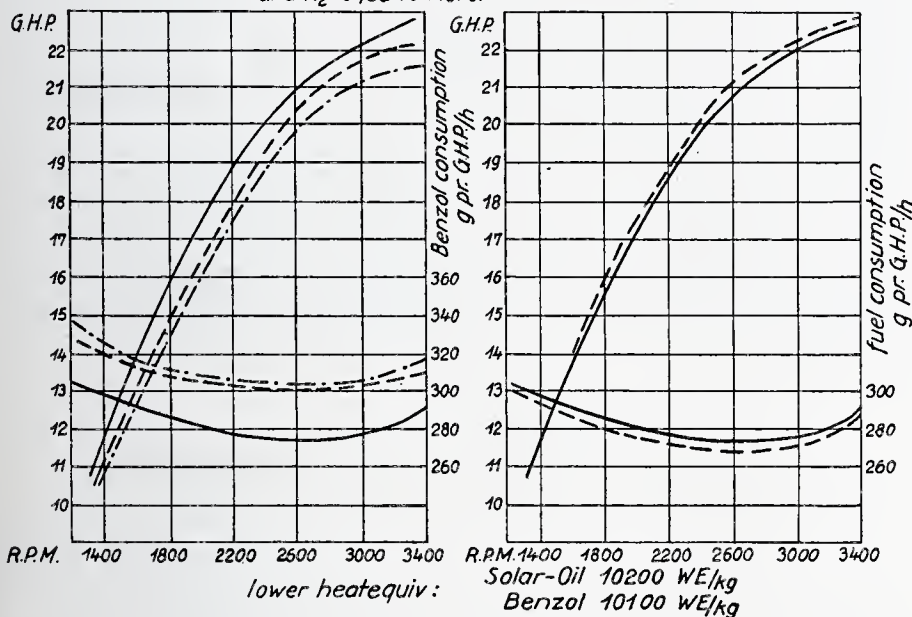


FIG. 6. GASOLINE MOTOR TESTS WITH ADDITION OF OXYHYDROGEN TO FUEL

Left: Gain in fuel consumption and power when operating with benzol.  
 Right: Comparison of fuel consumption and output when using benzol or Solar oil.

6. The cost of the buildings is reduced correspondingly. Besides, it is possible to operate the plants in the open air during winter and summer. The Berlin Pressure Electrolyzer described in Figure 4 is being so operated.

7. The power and operating costs of the compressor plants are eliminated.

8. Size and cost of catalyzing plants are reduced.

Returning to the first group of applications I may refer to the paper

read before this congress by Mr. Zur Nedden of the German Reichskohlenrat (German Federal Coal Council) and state that the transformation of coal into hydrogen for various purposes by means of the electric current fed into the pressure cell produces an especially flat rectangle for the chemical application of coal.

Where mechanical energy is gained directly by the use of electrolysis, the following may be said: While the great discoveries and inventions of Pathart, the I. G. Farbenindustrie, Geissen and Fischer, and especially of Bergius have enabled us to transform the heavy oil-components of the cracking-processes into motor-ready oil by hydrogenation in big plants, the electrolytic processes in question make the heavy oil motor-ready even for the normal high speed gasoline motor and this is done, not in big plants, not even through any change in motor design, but in the carburetor itself, thereby increasing the applications of the inventions of the great pioneers in the field of hydrogenation. Aside from the economic benefits involved by the use of oils instead of gasoline in motors, safety will be increased. I, for one, hope, for instance, that the burning up of passengers in the aeroplane service will become a regrettable incident of the past.

# SOME POTENTIAL RELATIONS BETWEEN ELECTRICITY AND COAL UTILIZATION

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## SUMMARY

In the following an attempt is made to estimate the nature of the fuel requirements of the future and what steps may be taken to meet these requirements.

It is concluded that solid fuels may largely disappear from the market and that demands will be almost exclusively for gaseous and readily gasifiable liquid fuels. Such fuels contain up to five times the amount of hydrogen contained in coal and therefore, to produce the desired fluid fuels without by-products and without losses, it will be necessary to decompose vast amounts of water in order to obtain the necessary hydrogen. In fact it is not unlikely that more water than coal will be used as raw material and that perhaps half of the energy of future fuel will come from the combustion of hydrogen obtained originally from water.

The decomposition of this quantity of water will release far more oxygen than that required to make the desired end products. Consequently it will be undesirable to draw upon air as a source of oxygen for coal processing since the hydrogen requirements must in any case come from water already yielding a large surplus in oxygen. The further increase in this surplus would result in an overbalanced production of oxygenated products, such as carbon monoxide gas, methanol, etc., unless a second process were introduced to restore the balance by reducing oxygenated material to hydrogenated products.

For the ideal processes the only materials used will be coal and water, all of which will appear in desirable products and none will appear as by-product and none will escape as flue gas. This ideal can be accomplished only by decomposing water in such a way that hydrogen and oxygen can be separated and directed into proper channels, where each will be used to the best advantage in the processing of coal and in the utilization of coal products.

In order to conserve coal and to keep coal requirements down to the minimum and in order to produce only the desired end products in

desirable proportions, it will be found that only a part of the required water can be decomposed by usual methods and that perhaps half must be decomposed by electricity. It is therefore concluded that coal processing will centre about water power plants, the entire output of which, in some cases, will not be electricity, but will be hydrogen and oxygen as already exemplified in the case of certain nitrogen projects—notably that of the 125,000 H.P. plant of the Norwegian Hydro Electric Nitrogen Corporation. In many such cases the hydrogen values will be sufficiently high to alone show profitable operation so that oxygen will appear at no cost, a circumstance which further precludes the use of air as a source of oxygen.

There is also a complementary electrical problem concerning means for developing 100 per cent load factors in operating plants and means for utilizing latent power resources not now in demand. Accordingly we have favorable circumstances for simultaneously solving problems relating to both coal and power in such a way that both coal and electricity can be used jointly in the one process of making fluid fuels. Thereby the highest degree of efficiency in utilization can be effected for each case and, instead of being competitive as at present, the two sources of energy, the one potential and the other kinetic, will be coöperated in the greatest general advantage.

### I. FUEL REQUIREMENTS OF THE FUTURE

As it is the purpose of this Conference to discuss essentially new developments, it may be advantageous to speculate somewhat upon certain circumstances which may affect the methods of utilizing coal in the future.

Since such a variety of new methods for coal processing are now rapidly developing, it naturally follows that there will develop more exacting demands for certain specific products of coal than could be supplied at the present time. Accordingly methods will be altered and continuously improved until it is possible to convert coal entirely and without by-products or waste into only those products in great demand. Therefore it will be interesting to estimate the nature of these future demands and to enquire how they would be met.

With more desirable forms of fuel available on all sides at competitive costs, coal as a raw fuel will gradually disappear from the market and, instead, it will be taken to large central plants as a raw material for the manufacture of the various products then in demand. It is

then not unlikely that the domestic and industrial consumer shall be in a position to dictate exactly just what products shall be made in his locality, just in what relative proportions solid, liquid and gaseous products shall be made and what their nature and composition shall be.

Already there are certain developments to indicate that solid fuels may gradually disappear from the market to be replaced by various fluid forms of fuel. Although domestic coke is used in vast quantities at the present time, few will question that the ideal form of domestic fuel would be gas if it could be delivered at competitive costs. At the present time the cost per therm of manufactured gas may run from ten to twenty times the cost of coal, but there is no reason why this should always be the case, and it is generally admitted that ultimately gas will be the universal form of fuel of the future. Already and in spite of present costs, many homes are heated by artificial gas or oil and, in Germany, there is the project already financed to supply cheap gas from the Ruhr over vast areas and distances in competition with shipments of coal.

So also with regard to the demand for metallurgical coke, there is evidence that new processes may be introduced to substitute those now using coke in vast quantities. For instance, there is to be noted a great deal of activity towards the reduction of ores to metal by means of gases instead of coke. Such developments have been reviewed in volume 51 (1927) of the Proceedings of the American Electrochemical Society, and in Bulletin 270 (1927) of the United States Bureau of Mines. Some such processes are already in commercial operation to some extent in Sweden and in Great Britain and it is significant that the United States Steel Corporation is erecting a plant at Cleveland for the reduction of 250 tons of iron per day by the Hornsey process and without the use of coke. In many quarters it is accepted that processes for making "steel direct from ore" by gaseous reduction will ultimately replace the blast furnace and with it the principal need for metallurgical coke.

There is therefore good reason for believing that the need for solid fuel in any form will ultimately disappear, perhaps gradually at first, but with accelerated momentum as the new methods are proven up. Substituting these solid fuels high in carbon and very low or free of hydrogen, the demand will be for gaseous and readily gasifiable liquid fuels.

## II. THE NATURE OF FLUID FUELS

The fluid fuels are very rich in free or combined hydrogen and are relatively low in carbon content. The liquid fuels will be composed of hydrocarbons or oxygenated hydrocarbons, such as various alcohols, and there will be also in demand liquid products other than fuel containing various alcohols, aldehydes, ketones, organic acids, etc., while the fuel gases will contain free hydrogen, hydro-carbons and carbon monoxide.

It is of course impossible to predict in what proportions the various products will be used since such proportions will vary with every locality and with every season, but in all cases the essential elements making up the products are carbon, hydrogen and oxygen.

The hydrocarbon compounds will be largely of the saturated series with the general formula  $C_NH_{2N+2}$  with the lighter members of the series in greatest demand. It is perhaps safe to generalize and say that the carbon-hydrogen ratio of all future coal products will average about 15 parts of carbon to 4 parts of hydrogen, whereas the raw material from which these products are to be made averages about 15 of carbon to only 1 of hydrogen. Therefore for every one ton of coal processed without waste or by-product, it will be necessary to provide 300 pounds of hydrogen gas by the decomposition of 2700 pounds of water.

The perfected processes of the future will then be operated entirely by internal firing in such a way that all the carbon and hydrogen of the raw material will appear in desirable end products and without loss in by-products or even in flue gases. On the average it appears that the charge will consist of 1 ton of coal to 1.35 tons of water and that the valuable products will weigh over 2 tons if nothing except coal ash is lost. In the ideal processes no other coal than that of the charge will be consumed and consequently there will be no flue gases or smoke. This ideal of course becomes possible when pure oxygen for internal firing is made available at low cost.

If we can accept a carbon-hydrogen ratio in future fuels to average 15 of carbon to 4 of hydrogen, it is interesting to note that the consumption of water as raw material will exceed that of coal as raw material and that, on burning these fuels, almost half of the energy will be generated by the combustion of the hydrogen originating from water alone. The problem of future fuel is therefore as much a question as to the best means for decomposing water as it is with regard to the best means to utilize coal.

It has been estimated above that for each 1 ton of coal used we will be decomposing 1.35 tons of water and that all the carbon and hydrogen will appear in the fuel products. With regard to oxygen, we may assume that coal contains 7.5 per cent and, since water contains 88.89 per cent, we have a total of 1.275 tons of oxygen in our raw material for each 1 ton of coal. If we assume that it is essential to have a ratio of 15 of carbon to 4 of hydrogen in the end products and 3 parts of the hydrogen come from water, it follows that we have a total of almost 26 parts of oxygen to deal with. This gives a final carbon-hydrogen-oxygen ratio in end products of 15-4-26, unless some of the oxygen is separated.

The constituents of desirable end products which can carry oxygen are carbon monoxide gas and various alcohols. It is not likely that the demand for these alcohols will total a very large percentage of all coal products and we might for the moment assume that practically all of the oxygen could appear only as carbon monoxide. In the ratio above established we have only 15 parts of carbon available and, if the future market should demand half of the in the form of hydrocarbons, then perhaps on the average only 7 parts are available for making carbon monoxide gas. These 7 parts of carbon are capable of combining with, roughly, only 9 parts of oxygen out of the total of 26 parts of oxygen, so that at least one-half or perhaps even two-thirds of the oxygen is surplus and cannot appear as a constituent of fluid fuels.

### III. SURPLUS OXYGEN

It is obvious from the above that coal and water are the only essential materials for coal processing and that their ratio of use will be definitely fixed by market conditions. In any case there is a real problem in finding how to deal with the surplus oxygen originating with the water needed in processing coal to make the various products in the proportions which will be demanded. If, as has been suggested, air were used as a source of free oxygen for coal processing, there would be a greatly overbalanced production of gas relative to liquid products and such gas would be far higher in carbon monoxide than is considered desirable, especially for domestic use.

There are two methods for dealing with surplus oxygen. The most obvious and desirable would be to separate it from the process so that the surplus could be used as, when and where desired. Otherwise it would be necessary to produce excessive amounts of carbon

monoxide gas and to burn coal to generate steam and to then have the carbon monoxide and steam interact for the production of hydrogen with the separation of carbon dioxide by a subsequent process.

It is evident that the best practice in coal processing will avoid the use of air or free oxygen from air and will restrict consumption to coal and water alone. It is also obvious that part of the water requirements will be decomposed before entering the process and in such a way that hydrogen and oxygen can be kept separate. The materials of manufacture then will include coal, water, hydrogen and oxygen, and with this basis it becomes possible to make hydrogenated or oxygenated liquid or gaseous fuels of any desired composition in any desired proportion, since any part or all of either hydrogen or oxygen can at any time be directed into other channels and uses.

#### IV. ELECTROLYSIS OF WATER

Theoretically, from 1 continuous Horse Power year of direct current power it is possible to produce about 70,000 cubic feet of hydrogen and 35,000 cubic feet of oxygen. The potential energy of this hydrogen is then equal to the kinetic energy of the electricity consumed and the pure oxygen is a free by-product.

The production of an electrolytic cell is proportional to the current (amperes) and a 10,000 ampere cell will produce per year 2,102,400 cubic feet of hydrogen and oxygen. If this cell were 100 per cent efficient, as above, it would have to operate at just about 1.5 volts and take no more than 20 H.P. years in electricity. However, in practice, it is essential to use higher voltage and the production per H.P. year then varies according to the following:

CELL VOLTAGE	PER CENT EFFICIENCY	CUBIC FEET PER KILOWATT HOUR	CUBIC FEET PER H. P. YEAR
1.5	100.0	16.0	105,786
1.75	85.71	13.71	90,669
2.0	75.0	12.0	79,340
2.25	66.67	10.67	70,524
2.5	60.0	9.6	63,716
2.75	54.54	8.75	57,696
3.0	50.0	8.0	52,893
4.0	37.5	6.0	39,670
5.0	30.0	4.8	31,736

When these figures are plotted it is seen that each 0.1 volt reduction has a different import and that it is progressively more and more important to save each succeeding 0.1 volt and that it is 25 times as important to save the ultimate 0.1 volt than it is at the highest voltage given.

Heretofore, it has been common practice, in fact necessary, to operate large capacity cells at voltages even as high as 3.0 volts since, without high voltage, production has been very small and, in some cases, impossible or impracticable. Although the process of electrolysis is exceedingly simple, it is a fact that heretofore no satisfactory cells of large capacity have been introduced commercially, and it is said that some of the most recent installations have had to be discarded.

Perhaps the most reasonable explanation of the destructive effect of high voltage is that chlorine gas is liberated. All caustic solutions available for electrolysis contain at least small traces of chlorides and, at voltages of over 2.5, nascent chlorine is liberated at the anodes. Such chlorine of course corrodes the anodes with the formation of soluble compounds of the metals. These metals are then precipitated by the excess caustic in the form of hydrates (or rust) and the caustic chlorides are regenerated to continue the cell destruction. Accordingly, a minute trace of chlorides in a cell at high voltage will work in cycles to the ultimate destruction of the equipment.

In practice the disadvantages of high voltage operation appear in many directions. Since 2.75 volt operation has not been uncommon, it might be contrasted with 1.75 volt operation. The saving of 1.0 volt per cell means 57 per cent greater output from the same power and practically eliminates the otherwise high costs in up-keep, repairs and amortization. On the other hand, on the basis of equal output, the wasting of 1.0 volt per cell requires 57 per cent greater investment in power plant, transmission and equipment for converting to direct current power in the cell room.

In an example using 100,000 H.P. in A.C. power, the saving of 1.0 volt per cell permits of the production of 8,100,000,000 cubic feet of hydrogen and oxygen per year instead of only 5,155,000,000 cubic feet. If hydrogen is valued at 50 cents per M. and oxygen is valued at 25 cents per M., the increased production can be valued at \$1,227,500 per year, representing interest at 6 per cent on a capital sum of \$20,000,000. From such data it can be estimated that the value of saving 1.0 volt on each 10,000 ampere cell is worth something like \$13,000.

## V. THE FUTURE COAL PROCESSING PLANT

For this we may picture on the St. Lawrence River, for instance, a water power plant developing 100,000 H.P. in D.C. power and feeding it directly into cells for the electrolysis of water for the production of 6,000,000,000 cubic feet of hydrogen and 3,000,000,000 cubic feet of oxygen per year. Adjacent to this site will be a large central station for coal processing and to it coal will be hauled for the manufacture of fluid fuels. In addition there will grow up around this site a variety of industries attracted by low cost fuel gases and by low cost oxygen for combustion—in other words, for low cost high temperature heat. From the site surplus fluid fuels will be shipped by pipe lines and tank cars to towns and cities over a wide area.

The electrolytic hydrogen will be available directly for such purposes as the reduction of ores, the synthesis of ammonia, the liquefaction of coal, etc., or it may be used as a fuel gas alone or mixed with other fuel gases and sent to industrial and domestic consumers. All these uses for hydrogen require no comment, but it might be again emphasized that the use of 6,000,000,000 cubic feet of electrolytic hydrogen will substitute for the consumption of about 250,000 tons of coal for making fluid products.

Many processes are being developed for the reduction of ores by gases and therefore the peculiar advantages of hydrogen for such purposes may be mentioned. Electrolytic hydrogen has the advantage that it is of great purity and that it is the ideal reducing agent. It not only reduces oxide ores with facility at low temperature, but it also is capable of picking up sulphur and phosphorus and carrying these impurities off in the gas stream. The furnace gases are readily freed of water, hydrogen sulphide and phosphine, so that surplus hydrogen can be recirculated to its complete utilization. The metal product is free of silicon, sulphur, phosphorus, and carbon and represents the production of steel direct from ore in simple apparatus of negligible first cost.

The 3,000,000,000 cubic feet of oxygen produced in the cited illustration will be available for the low temperature carbonization of coal, the complete gasification of coal, for the production of water gas for methanol syntheses, for high temperature combustions in industry, and for the operation of blast furnaces and smelters.

Coal may be gasified in apparatus resembling a blast furnace, operated with an oxygen-steam blast, the ash being withdrawn as slag. The difference in operation between this apparatus and the

ordinary large gas producer would be chiefly in that the absence of nitrogen will permit of the injection and decomposition of a larger amount of steam and of the production of 400 B.t.u. gas instead of lean producer gas. As estimated by various authorities, the efficiency should be over 95 per cent since even the ordinary producer will show up to 80 per cent efficiency from the use of air.

The conditions for operation of this apparatus should be ideal for the low temperature carbonization of the coal in that the coal will slowly descend countercurrent to an ascending column of hot water gas. The volatile matter of the coal released at one temperature would be washed back and upward into cooler zones and preserved from decomposition. It is possible also that the apparatus could be adapted for the abstraction of part of the water gas formed at the base so that, in a single process, it may be possible to produce from coal recoverable liquids, rich fuel gases and water gas for the synthesis of alcohols, etc.

Supplies of low cost oxygen may also provide the best means for the carbonization and gasification of almost any form of pulverized carbonaceous material, such as coal, lignite, tars, oil, peat or even straw. Such material in a finely divided condition could be permitted to drop by gravity through ascending columns of hot reducing gases free of nitrogen, the equipment being so arranged that operations are completed during the brief period in which the minute particles are in suspension. The process may be operated to produce char for boiler feed as in the case of the McEwen-Runge process of the International Combustion Engineering Corporation, or to complete gasification as in the case of the Bourcoud process. It is most significant that both Runge and Bourcoud have pointed out the desirability of operating such processes with oxygen.

From the water power site oxygen could also be delivered in pipe lines for air enrichments for high temperature processes such as the melting of metals, the production of cement, glass, porcelain, refractories, abrasives, brick, tile, etc. The possibilities of oxygen for such purposes are well illustrated in the use of oxy-acetylene and oxy-hydrogen torches for cutting metals and there is no reason why lesser proportions of oxygen could not be used in basic processes of the metallurgical and ceramic industries.

It is reasonable therefore to picture a variety of industries capable of absorbing vast amounts of electrolytic hydrogen and oxygen centering about water power sites. Already there are many instances

where large blocks of power are used to produce electrolytic hydrogen for nitrogen fixation. In the case of the Norwegian Hydro-Electric Nitrogen Corporation 125,000 H.P. are being used for such purposes, and if all such new projects were totalled it appears that shortly 1,000,000 H.P. will be required in nitrogen plants alone. In all these cases hydrogen alone will be used and oxygen will be a by-product of no cost. The development of uses for oxygen in coal processing and in combustions will undoubtedly result in new developments as previously pictured.

The principal products of the combined coal processing and power plant will include fuel gases, various grades of liquid fuels and hydrogen and oxygen gases. The demand for these products will be influenced by the change of season and, in order to maintain constant operating conditions on the main equipment, production may be shifted from one product to another. The power and electrolytic cell plants will be operated at constant load for a steady production of hydrogen and oxygen throughout the year. During mid-winter much of the hydrogen and oxygen will be used in gas making, but as the gas load decreases there will be a complementary increase in the production of liquid fuels and various solid and liquid products such as fixed nitrogen, crude reduced iron and other metals, various solvents and other products convenient for storage. Much of the equipment for producing these crude products will be relatively low in cost so that it can economically be idled during the winter season while finishing processes can be operated steadily throughout the year on stocks of crude material. Thus in some such way it will not be difficult to take care of seasonal variations in demand or to utilize off-peak capacities on power plants.

## VI. THE POWER ASPECT

There is also a complementary problem of the electrical industry as indicated by the facts that—

1. In North America alone some \$20,000,000,000 are invested in enterprises supplying electricity in a market capable of absorbing only about half of the possible output.
2. In North America there remain undeveloped some 75,000,000 maximum horse power in water power.
3. There are many sites where steam power could be developed at costs comparable to water power if use could be made of the output.

#### 4. Similar conditions exist throughout the world.

These facts seem to indicate that there is a wide field for the cultivation of new uses for power in order to, first, establish 100 per cent load factors on existing plants, and, second, in order to draw upon undeveloped resources in energy. The opportunities lie in devising methods so that electricity can be coöperated with coal in providing the fuels of the future and means for perfection in their use. It would be difficult, if not impossible, to name any other vehicle than the electrolytic cell for meeting all requirements of the case.

Electrolytic cells can be automatically operated in small space and at high efficiency at capital cost of only a few dollars per H.P. and with all operating costs totalling less than \$5 per H.P. year. Such costs mean less than 5 cents per thousand cubic feet of hydrogen and oxygen and, to this, power adds 1.1 cent for each \$1 cost per H.P. year.

With hydraulic power plants having surplus water there may be no extra costs for using off-peak capacity and such power companies could produce the gases at about 5 cents. Similarly, power companies operating steam plants could utilize surplus capacity at virtually the cost of extra coal only and produce the gases under 25 cents. As for the use of continuous power at water power sites, all costs should average around 20 cents. If all these costs were imposed on hydrogen the figures would vary from 8 to 38 cents and oxygen would bear no cost whatever.

To the large scale electrolysis of water there is an analogy in the electric steam boiler, operated in Canada to a total capacity of 750,000 H.P. Although the demand for steam is narrowly restricted, largely to paper mills, and although the value of the power so used is only about \$7 per H.P., it is said that "this invention has made possible the development of the Gatineau and Saguenay Rivers." If that is true, then the electrical industry has a lot to look forward to in the electrolysis of water, instead of boiling it, in order to supply hydrogen and oxygen for the scientific processing of coal.

In the present markets kinetic energy, as electricity, competes with potential energy in the form of solid, liquid and gaseous fuels, and in many cases this competition is already quite keen. For instance, motor cars and buses severely compete with street cars and suburban electric railways, and domestic gas competes with the domestic uses of electricity. In view of recent developments it is not unreasonable to expect that gas may be delivered at such costs that it can compete

with solid fuels and become the form of fuel in universal demand. The delivery of gas at such low costs would be bound to seriously affect the sales of electricity for a great variety of domestic, industrial and municipal purposes.

It is possible that, in the future, it may be considered most undesirable to use "raw electricity" just as it is now considered undesirable to burn "raw coal." Just as coal is being looked upon more and more as a raw material for the manufacture of coal products, so electricity may be looked upon as a raw form of elusive kinetic energy which should be harnessed in some way. The opportunity to do this is offered in the application of electricity with coal in the production of gases and liquid fuels of low cost.

## FUEL TESTS AND PLANT OPERATION

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The testing of solid fuels serves several purposes. It adds to scientific knowledge of the fuel substance; and it procures data which are required to control and operate plants in which the calorific power stored in the fuel is converted into another form. This paper deals only with those tests and observations which serve this latter purpose. By this I mean that only such fuel tests will be included as have a direct application to plant operation and meet operating conditions. Beyond this I intend also to discuss several new viewpoints regarding the possibility of plant control on the basis of coal and fuel analysis.

The operating requirements of a plant demand, first of all, quick determinations, not only because "time is money," but also because the results of the tests can have their full effect on the control of plant operation only when they are at the disposal of the supervisor at the proper time. With this end in view we have in the first place made an effort to reduce the time required for one of the most important fuel tests, i.e., the determination of moisture. The old method hitherto almost universally used for the determination of moisture in solid fuels, by weighing before and after drying, takes about two hours. Treating fuel with xylene and determining the moisture by subsequent distillation takes an average of 45 minutes. We have been successful in working out a method, the results of which are equally reliable, and which will not take more than 8 minutes' time.

Considerable difficulties were encountered in our endeavors to split up the coal substance by new methods. The usual way of utilizing bituminous coal may be considered as a process of heat conversion. The basis and the range of this process are primarily defined by the amount of heat stored in the fuel, i.e., by its calorific power or value. The calorific power, however, indicates only the total amount of the usable heat but does not permit any deductions as to the *kind* of conversion of the fuel. It is well known that this kind of conversion is in a high degree dependent upon the distribution of the energy of the coal between volatile and non-volatile substances. The relative proportion of both these substances forming the fuel

plays a very important part not only in burning the raw fuel but even more so in generating heat from pulverized coal. In fact, it plays a most important rôle in every kind of fuel utilization.

The usual short or proximate analysis of coal offers an easy way to split up the coal substance into moisture, fixed carbon, ash and volatile matter, the latter being determined by difference of weight. The results of this test give an only approximate insight into the nature of the fuel; or, it would be better to say, they *appear* to give only such an insight because the results of these tests have a very doubtful value for the deduction of reliable calculations and therefore can be applied only within very narrow limits.

We are using a process which in its extent is predetermined by a certain amount of heat that can be measured in calories; and the proximate analysis is characterized by giving the results in per cent by weight for the different parts of the determination, so that we talk about "per cent by weight of volatile substances" or gases, while only their calorific value or power really serves as a reliable comparison. This leads at once to the conclusion that the short or proximate analysis does not form a suitable basis for the proper characterization of fuels.

In this connection we have tried to follow a new path by dividing the heat stored in the fuel into the three single phases "solid, liquid and gaseous" corresponding to the products of the destructive distillation of coal: coke, tar and gas. These products are always yielded whenever coal is being heated, irrespective of whether it is consumed by burning it in a fire or by converting it by other means. This *division* of the heat contained in the fuel into the three single phases "solid, liquid and gaseous" offers a way to determine, irrespective of the kind of fuel, a clear and reliable basis for predicting the possibilities of the conversion of fuel of every kind by combustion, distillation or total gasification.

In reality the above new method amounts only to combining a number of fuel tests which are already in use. We have however standardized these methods in such a way that *all results obtained in the determination of the fuel are expressed in common values representing the converted heat.*

Until now we have had to use a combination of the following methods: low temperature distillation, tube distillation and crucible test, although a combination of these methods is really not admissible either from the scientific or the practical point of view. We deter-

mine the contents of tar in the fuel by a low temperature distillation; we obtain the contents of fixed carbon by a crucible test and the contents of gas by the tube distillation according to a method proposed by the late Professor Strache. The latter test, which I will discuss in a moment, does not determine the volume or weight of the gaseous constituents of the coal but their content of heat is expressed in calories. While the tests for determining the primary tar by low temperature distillation methods are well known as are also the crucible tests, the tube test introduced by Strache may not be sufficiently known on this side of the ocean, so I will give you a short outline of it.

### FUEL DISTILLATION IN THE STRACHE TUBE

This method makes use of a tube made of refractory glass with thick walls and an internal diameter of not less than 6 mm. After the tube has been well dried and weighed about one-tenth of a gram of fuel is introduced to rest in the bottom of the bend. The air in the tube is displaced by nitrogen and the inclined end of the tube is drawn to form a capillary and closed. The U-part of the tube serves as a condenser for tar and water and for this purpose it is submerged in a beaker filled with water and its open end is directly connected with a Strache gas calorimeter for the reception of the gas. The coal is gently heated and when the process of distillation is brought to an end which requires only a few minutes, the closed capillary is broken and the entering air forces the gas remaining in the tube into the calorimeter attached to the other end of the tube.

To determine the amount of tar, the tube is disconnected from the calorimeter, cut off, and the remaining U-tube is brought into an exicator to dry up the water. After complete evaporation of the water the tube is weighed and then washed with chloroform to dissolve the tar and again weighed; the difference in weight indicates the amount of tar formed by the distillation of the fuel. The gas in the calorimeter is subjected to combustion and the calories indicated are noted.

The above description will serve only as a brief explanation of the principle of the method and the many alterations which from time to time have been suggested will be left out of consideration here. After this short digression let me return to our main subject.

In trying to combine the results of the different tests which I mentioned above and which are based upon widely different methods, insurmountable difficulties are experienced for the simple reason that the results obtained lack a mode of comparison. In the low

temperature distillation test a maximum yield of tar is obtained but only part of the gas, while the residue in the retort cannot be taken as fixed carbon since it contains still an undefined amount of combustible gases. On the other hand in the crucible test heavy overheating and resulting decompositions of the tar vapors cannot be avoided and therefore a determination of the gas yield is impossible with this test. Furthermore, the weight of the coke comes out too high owing to carbon deposits formed by the decomposition of tar vapors. By the Strache tube test a reliable tar yield is obtained and also the gas amount is fairly correct if a sufficiently high temperature has been applied, but the amount of fixed carbon cannot be determined by this method.

It appears therefore that it is absolutely necessary to determine the contents of moisture as well as the yield of tar, gas and coke in *a single test*. Furthermore it is highly desirable to obtain for each single distillation product the amount of heat which it represents in order to facilitate further deductions. A new form of fuel determination which serves this purpose will be described by me later on and I believe that this test will perhaps interest you also for other reasons.

As you know the ultimate or combustion analysis of fuels represents a method which does not give complete satisfaction inasmuch as the oxygen is determined by difference so that every error in the determination of the other constituents must naturally reflect upon the result obtained for the oxygen. The rather small amounts of hydrogen generally present will easily lead to errors in this test. The contents of hydrogen in a fuel play a very important part in its conversion, as well as serving as an indication of its geological age upon which depends its natural carbon enrichment. It is only natural that efforts have been made to make this test more accurate, but all endeavors to find a direct method for the determination of the oxygen have so far not been successful; and our own experiments with method suggested by various people have yielded only negative results. Also in this connection we have developed new methods which will be touched upon in the last part of this paper.

The methods which I suggest for the testing of fuels differ from those generally in use up to the present time, mainly in that they secure the complete recovery of the gaseous distillation products and their determination as to quantity and composition. The use of the gas analysis in our methods leads to quite new and surprising results which promise to offer new and improved methods of the running control of plant operations.

Allow me to give you now a brief outline of the methods which I am applying:

1. The *quick determination of moisture contents* is based upon the following reasoning: If a more or less powdery fuel containing moisture is soaked in approximately absolute alcohol and allowed to rest for a while, a balancing exchange between alcohol and water takes place resulting in the formation of diluted alcohol. As can be easily proved by a test the composition of the liquid above the fuel is exactly the same as that of the liquid absorbed by the coal. By warming the flask containing the fuel and the alcohol up to a temperature nearly approaching the boiling point of the alcohol, the time required to obtain the balance between water and alcohol can be reduced to a few minutes. In taking measured quantities of coal and alcohol for the test, the water contained in the fuel can easily be ascertained by determining the dilution of the alcohol which has taken place. For instance, if 20 grams of coal containing 20 per cent of moisture are soaked in 100 grams of absolute alcohol (100 per cent), 104 grams diluted alcohol with a water content of 3.84 per cent will be determined and the contents of alcohol in the liquid will have been reduced from 100 to 96.16 per cent. To determine the contents of moisture in the coal treated, it is necessary to ascertain with a sufficient degree of accuracy the amount of water taken up by the originally anhydrous alcohol. It is, of course, not necessary to test the whole quantity but only a measured part of the solution: For this purpose the usual method of testing the specific gravity of the alcohol is neither applicable nor sufficiently accurate since the variations in the concentration of the alcohol are relatively very small. The most successful and accurate method for this purpose is the determination of the cryohydric point which is done as follows:

A mixture of equal parts of absolute alcohol of 100 per cent and pure kerosene will form at normal room temperature a fully homogenous liquid. If this mixture is gently cooled it becomes turbid at a certain temperature which can be exactly determined. This temperature marks the beginning of the separation of alcohol and water contained in the liquid and is in relation to the proportion of water contained in the alcohol, provided that only kerosene of the same quality is always used in the test. The temperature of separation indicated by the turbidity of the mixture varies slightly with the quality and composition of the kerosene, applied so that for the different kinds of kerosene special curves for adjustments must be plotted to which I will refer later.

With increasing water content of the alcohol the temperature of separation also increases rapidly so that for a water content of about 10 per cent, corresponding to an alcohol of about 90 per cent, the temperature of separation approaches the boiling point, while with absolute alcohol the temperature of separation is indicated considerably under the normal room temperature.

This shape of the separating curve equals practically a straight line and each 10°C. of the separating temperature correspond to about 1 per cent of water in the tested alcohol. From this observation it can be deduced that the suggested method is applicable for the determination of very small proportions of water in the alcohol; and some time ago we applied it also to determine traces of water in so-called absolute alcohol.

If the proportion of the applied quantity of alcohol to the quantity of coal and the moisture contents of the latter is predetermined so that the variations of the water content in the alcohol after the treatment of the coal do not exceed 0 to 10 per cent, the determination is simple, quick and accurate.

To test a coal for moisture in this way, the powdered fuel is introduced into a small bulb flask with ground stopper which is provided with an ascension tube. The sample is then soaked in 100 grams of absolute alcohol. The flask with contents is then heated almost to the boiling point and then quickly cooled. Twenty cubic centimeters taken from the clear solution above the sample in the bottom of the flask are mixed with 20 cc. of kerosene in a special test tube. This test tube of rather wide diameter holds inside a thermometer with a scale divided into tenth of degrees Centigrade. The tube is further provided with a stirring arrangement with vertical movement. The mixture introduced in this tube is warmed and at the same time rigorously agitated by the stirrer until a homogenous mixture is obtained. The tube, while further agitating its contents, is then cooled until a turbidity of the mixture becomes apparent and at this moment the temperature is noted, which corresponds to a certain amount of water contained in the alcohol and, after calculation, to the moisture held by the sample of coal tested. When treating lignites which are rich in bitumen, some of this goes into solution in the alcohol and causes a yellow discoloration which, however, does not affect the result of the test.

A comparison of a number of tests carried out by the xylene method and by the new alcohol method are given in Table I. The

determination can be easily completed within ten minutes and the time required can be further shortened by applying a special thermometer the scale of which is specially graduated to show directly the contents of water for a given amount of coal applied.

Our method for the *determination of moisture, yield of tar, gas and coke in a single test* has been developed to replace the present combination of the proximate analysis of coal and the low temperature distillation test. Our test is carried out as follows:

About 20 grams of coal are reduced to pea size and dried with the exclusion of air in a slow stream of nitrogen or carbon dioxide. The water thus expelled is collected and determined. After the gas stream has been stopped the coal remains undisturbed in the apparatus and is immediately distilled by applying so low a temperature

TABLE I

SAMPLE	CONTENTS OF MOISTURE	
	Xylene method	New method
I	15.5	15.6
II	15.3	15.1
III	45.0	44.8
IV	4.8	5.0
V	44.0	43.9
VI	11.8	12.1

that the maximum yield of primary tar is obtained. This distillation, however, is not terminated after the charge has reached the usual 530°C., but a temperature of 1000° to 1100°C. is reached in a further distillation step so that a coke residue remains which is practically free from volatile constituents. During both steps of the distillation, at low temperature up to 530°C., as well as during the application of the high temperature from 530° to 1100°C., the gases developed are separately collected and their quantity, composition and calorific value is determined. If necessary the results can to a certain extent be checked by ascertaining the specific gravity of the gases. By this new method of analyzing fuel the following particulars are ascertained:

1. The moisture in the fuel.
2. The chemically formed water obtained during distillation of the fuel.

3. The maximum yield of tar: also the yield of primary tar.
4. The yield of gas when distilling up to a temperature of 530°C.
5. The yield of gas while distilling the fuel at a temperature between 530° and 1100°C.
6. The quantity of the coke residue which may be taken as a mixture of fixed carbon and ash, practically free of volatile constituents.

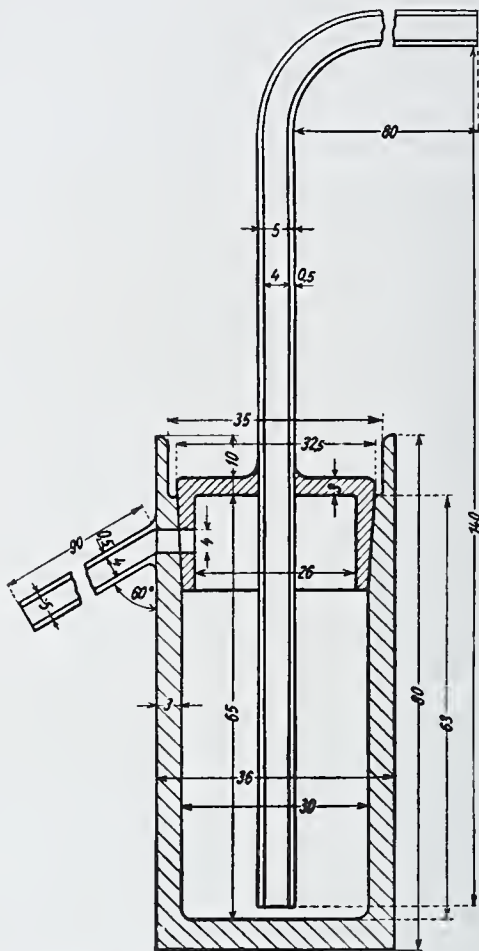


FIG. 1. SPECIAL STEEL DISTILLATION RETORT FOR NEW FUEL TEST

From the above items 4 and 5 the total yield of gas can be calculated. The apparatus used for this test is shown in Figure 1 and it consists of a retort made of Krupp's special V2A steel with thick walls. On one side an offtake tube is provided for the escape of gases and vapors while the top of the retort is closed by a lid with a tapered rim. This lid holds a tube reaching to the bottom of the retort for

the introduction of gases into the coal for drying same, as indicated above. The joint between lid and retort can be rendered absolutely tight by filling the cup formed above the lid with molten lead. For the normal test this latter precaution is not required but it forms a useful adjunct when testing the coke residue for its absorptive capacity. To do this the coke must be cooled under vacuum.

The end of the offtake pipe is introduced into the neck of a small bulb flask which, being cooled from the outside, collects the tar and the water chemically formed during the distillation. The non-condensable gases are conducted by air-tight connections from the flask



FIG. 2. WIRE COILS FOR HEATING THE DISTILLATION RETORT FOR NEW FUEL TEST

to gas holders and are stored therein. The collection of the gases takes place by allowing an equal stream of water to run out of the gas holders, and the adjustments must be made very carefully so that neither pressure nor suction is apparent in the retort. To control this, a mercury gauge is connected to the gas pipe of the testing set. To assure an even increase in the temperature of distillation and to enable an easy adjustment at any time, the retort is heated in an electric furnace which, with its electric heating wire coil, is shown in Figure 2, while Figure 3 shows the collecting flask and the whole arrangement set up for a test.

The charged retort is first of all connected to a cylinder containing calcium chloride and when dealing with fuels with rather high moisture contents like brown coal, peat or lignites, the calcium chloride cylinder is provided with a collecting chamber for the discharged water. The sample in the retort is dried in a slowly travelling stream

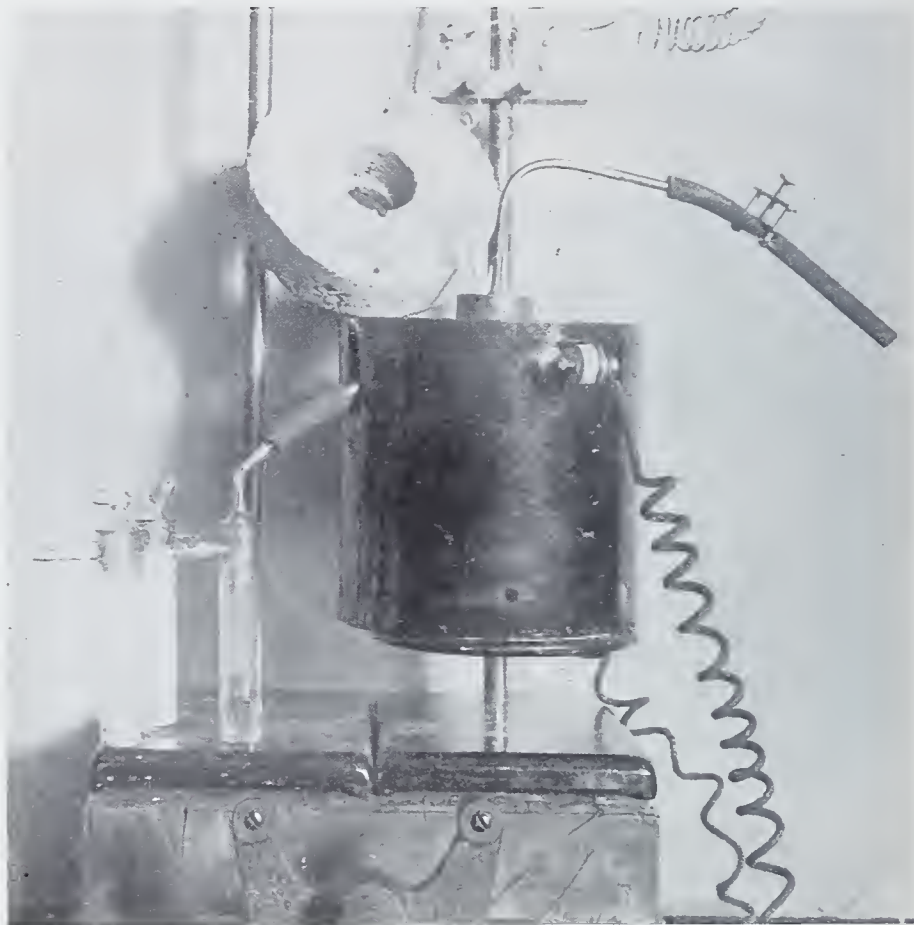


FIG. 3. ARRANGEMENT OF COMPLETE APPARATUS FOR NEW FUEL TEST

of nitrogen at  $105^{\circ}\text{C}$ . and after drying is concluded the distillation is immediately commenced to prevent an admission of air to the coal in the retort.

#### DEDUCTIONS FROM THE RESULTS OF THE TEST

Owing to the comparatively large size of the sample treated (20 grams) and to the fact that the fuel need not be ground finely, the

determination of the moisture is very accurate. A predrying process accompanied by an absorption of oxygen from the air, which may affect the ultimate results of such fuel tests with lignite as well as with true coal, is not applied in this test. The determination of the chemically formed water by the uniting of hydrogen and oxygen at elevated temperatures is very useful for all such cases where in processes of heat conversion the heat economy is to be controlled by calculation. The knowledge of the amount of chemically formed water of a fuel also allows one to judge its composition as far as it depends upon its geological age. Furthermore, by knowing the amount of water formed by chemical combination, the loss of heat from water vapors in the gases can be calculated, and used in obtaining the net calorific value.

The exact determination of the total gas volume produced, the composition of the gas and its calorific value, enable one to calculate the proportion of heat of the analyzed fuel recoverable in the gaseous state; by gaseous heat proportion is meant the amount of heat which by distilling the fuel can be recovered in the form of permanent gases, leaving a coke residue practically free from volatile constituents and avoiding a decomposition of tar vapors during the test. Some time ago the late Professor Strache introduced the expression "gas heat value index" (Gasheizwertzahl) by which he intended to express the amount of heat per kilogram of fuel which was available as permanent gases when at the same time the primary tar was recovered by distillation. We intend to use the calorific value of the fuel as a basis from which to calculate the proportion of the total calorific value expressed in per cent, which is recoverable in the gaseous state. This represents the first step in the direction of allocating the heat contained in the fuel.

To show the practical effect of characterizing a fuel in such a way the following example may be mentioned. A low temperature coke may contain, for instance, 4.3 per cent of heat recoverable in the form of gas. When burning this coke on a grate or in dust firing, 4.3 per cent of the total heat which it contains, will, in the heat conversion process, be burnt as gas while the remaining 95.7 per cent of the heat will be developed from the solid coke. According to the proximate analysis the same coke fuel contained 25 per cent of volatile matter, and from this comparative example it can be deduced that the proximate analysis does not yield any reliable figures by which the conversion of the heat can be judged. On the contrary its results may lead

to quite erroneous conclusions in that it shows the proportion of volatile constituents much greater than one is justified in assuming, when, for instance, the fuel is consumed in an open fire.

With bituminous fuels these conditions are somewhat more complicated due to the presence of tar. The total heat stored in the fuel must in this case be allocated to three components: the gaseous heat, the tar heat and the coke heat so that we have to distinguish between

TABLE II

SAMPLE	GAS HEAT PROPORTION	COKE HEAT PROPORTION	TAR HEAT PROPORTION
Brown coals			
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
IV	19.6	69.6	10.8
III	18.3	73.7	7.7
XII	16.3	74.3	9.4
II	16.1	71.0	12.9
IX	15.9	71.2	12.9
VII	15.5	64.6	19.9
XI	14.3	63.1	22.6
VIII	14.3	72.3	13.4
I	13.4	56.5	30.1
X	12.0	64.9	23.1
True coals			
4	17.8		
5	16.7		
2	16.4		
6	13.1		
3	12.1		
7	11.8		
8	11.4		
1	11.3		

the gas heat proportion, the coke heat proportion and the tar heat proportion. These quantities of heat added together amount to the 100 per cent of the heat value represented by the fuel.

In Table II is given an example for the allocation of the heat values. The proportion of coke heat has been calculated from the amount of coke and the calorific value of the fixed carbon taken at 8130 calories, and in addition it has been determined by a bomb calorimeter. Gen-

erally the calculation will quite suffice since we are dealing here with a coke which is practically free from volatile constituents and can be taken as a mixture of fixed carbon and ash. The proportion of heat which is to be attributed to the tar must be calculated by difference in adding the coke heat and gas heat and this figure subtracted from 100 per cent, the latter representing the total calorific value of the fuel.

I cannot here go further into these details, with which I shall deal in a later paper, but it will suffice to draw your attention to the fact that with this suggested form of fuel analysis the second purpose also is reached, i.e., the allocation of the coal substance to gas, coke and tar, not by per cent of weight, but in the form of heat proportions, which is certainly a more adaptable basis for the use of the fuel or the conversion of the heat therein.

We obtain the required figures in the following way:

1. We determine the calorific value of the fuel.
2. We determine:
  - a. Amount of gas by distillation in cubic meters per 100 kilograms of coal: distilled up to 1100°C.
  - b. Composition of gas in per cent by volume.
  - c. Calorific value of gas in kilogram calories per cubic meter: (1) calculated from its composition, (2) checked by its specific gravity, (3) determined with a calorimeter.
3. From 2a and 2b can be calculated the amount of gas in cubic meters per 100 kilograms:

*Amount of gas in cubic meters per 100 kgm. multiplied by the calorific value per cubic meter divided by 100 = gas heat value index*

This value represents the amount of heat which can be recovered in the form of gas per kilogram of the fuel tested. This leads to the following equation:

$$\frac{\text{gas heat value index}}{\text{calorific value of fuel}} = \text{proportion of the heat in form of gas in per cent}$$

This value represents the percentage of the heat of the fuel which will be available in the form of combustible gases when the fuel is being distilled so that decomposition of the tar is altogether avoided and at the same time a coke residue is obtained which is practically free from volatile constituents.

Table II shows the gas heat proportions of a number of widely

differing fuels and it should be noticed that the Roman figures refer to the different seams of a single lignitic brown coal deposit while the other figures stand for a number of widely varying true coals taken without particular selection.

We know that with the increasing geological age of coal its proportion of fixed carbon is gradually increased by reactions taking place under natural influences. This process we may perhaps term natural carbon enrichment and the degree it has reached at the time of mining the coal is a basis for its composition and its classification among fuels.

In the analytical method which we have suggested above, we have also a sure means of determining the degree of natural carbon enrichment of each fuel. As an example we give Table III the results obtained from tests of coal originating from deposits at Ostrau in Czechoslovakia.

TABLE III

	KARWIN SEAMS	UPPER OSTRAU SEAMS	LOWER OSTRAU SEAMS	
			Upper part	Lower part
Calorific value of pure coal, kgm. Cal.....	7794	8250	8440	8456
Proportion of gas heat, per cent.	12.4	11.4	11.3	9.5

This last value of 9.5 per cent will probably represent the lower limit of the gas heat proportion of true coals as far as they may not rightly be called anthracite. In comparing the figures of the table it is interesting to note the gradual increase of the calorific value in relation to the natural carbon enrichment and at the same time the gradual decrease of the gas heat proportion in favor of a rapidly increasing coke heat proportion. It is, however, rather surprising that the gas heat proportions of the whole fuel series do not show very wide variations as might be assumed at first and that in this respect there are no far-reaching differences between brown coal and true coal. This can serve as a further proof of the correctness of the genetic comprehension of the whole fuel series as far as humic fuels are concerned.

A study of the gas heat proportions will be of particular interest in connection with processes by which either the carbon of the fuel is increased by subjecting the fuel to such gentle heat in retorts that

no tar is formed, or by which the fuel is treated in a low temperature carbonization process so that the whole tar or part of it is obtained. The effect of such treatment of a lignite similar to the deposits in Dakota may be gathered from Table IV.

In order to convert lignite into bertzit the lignite is distilled at a temperature of 280°C., so that no tar is formed, while for obtaining karburit a higher temperature is applied so that small amounts of tar are formed. The fact that in the case of bertzit, in spite of the treatment by distillation, the proportion of gas heat has increased, is rather surprising, and I may return to the subject in the course of the discussion. As a rule the proportion of gas heat is, of course, reduced by distillation treatments and it stands to reason that low temperature coke has a lower proportion of gas heat compared with the fuel from which it has been obtained. The 8.3 per cent of gas heat pro-

TABLE IV

	LIGNITE	BERTZIT	KARBURIT	LOW TEMPERA- TURE COKE
Proportion of gas heat, per cent.....	13.9	16.8	7.5	8.3.

TABLE V

	I	II	III	IV
Proportion of gas heat, per cent.....	4.3	4.4	2.8	10.4

portion in the low temperature coke previously mentioned must be considered rather high; it is nearly as high as for the good bituminous coals referred to previously. From this comparison we can draw the deduction that by burning this low temperature coke the same results will be obtained as are secured from bituminous coals of the lower Ostrau seams which I have mentioned previously. We must of course, take into consideration the structure and surface of both kinds of fuels, which, however, I do not intend to discuss in this place.

In the case of low temperature cokes we find large differences in their composition which are dependent upon the conditions under which the fuel has been subjected to low temperature carbonization. Although this fact is well known I want to illustrate it by some figures obtained from tests made on low temperature cokes manufactured in a commercial plant from brown coal, the quality of which was practically identical in all cases. (See Table V.)

The comparison of these results leads to an important deduction which is perhaps not always taken sufficiently into consideration. In all cases referring to raw fuels as well as retort residues or cokes it should always be taken into account that the proportion of gas heat is comparatively small, amounting at its highest to about one-fifth of the total calorific value and being reduced to a few per cent only in the case of cokes. When we consider these facts it will become quite clear that the combustion and gasification of solid fuels is mainly dependent on the conditions under which the coke residue can be burned or gasified. This fact is especially important in the combustion of coal dust, since here the combustion is mainly influenced by a conversion of the coke residue. This conversion takes a certain time and therefore requires well and amply proportioned combustion chambers as opposed to the speedy combustion of the gaseous parts of coal dust.

The allocation of the calorific value of a fuel to proportionate gas heat, coke heat and tar heat means in a sense also the subdividing of the combustion process into the combustion of gas, of coke and of tar respectively. Even more important appears the possibility of making the following deductions concerning the use of the fuel:

In relation to the process of *carbonization* we are in a position to deduce particulars as to the amount of heat available which can be liberated in the form of combustible gas by distillation. This refers to the low temperature carbonization for the recovery of a primary tar as well as to high temperature carbonization in coke ovens and gas retorts. In the latter instances, however, we must take into account the fact that a certain proportion of tar is being decomposed by the process. In relation to the total gasification we are in a position to deduce particulars as to the amount of heat which can be recovered as distillation gas of high calorific value and also particulars on the amount of heat recovered in the form of producer gas of low calorific value or as water gas. These data create the basis for exactly calculating the gasification process as to quantity, composition and calorific value of the recoverable gas. Let me illustrate these statements by presenting a calculation which refers to the production of rich gas by fuel gasification in a producer:

The coal on which this calculation is based gives the following results in proximate analysis:

Moisture.....	2.9 per cent
Ash.....	10.8 per cent
Fixed carbon.....	58.0 per cent
Volatile matter.....	<u>28.3 per cent</u>
	100.0 per cent

Calorific value.....	7570 Cal.
Gas heating value index, 1362 Cal.; gas heat proportion.....	18.0 per cent
Coke heating value index, 5120 Cal.; coke heat proportion.....	67.7 per cent
Tar heating value index, 1080 Cal.; tar heat proportion.....	14.3 per cent
Calorific value (calculated).....	7562 Cal.
Calorific value (determined).....	7570 Cal.

The calorific value of the gas is calculated as follows: 100 kilograms of coal yield 20.3 cubic metres of distillation gas with a calorific value of 6720 calories per cubic meter. The composition of the gas and the calculation of the composition of the final rich gas shall not be considered here; these calculations are well known and would take up too much space. From the above figures the following theoretical deductions can be made:

100 kilograms of coal yield:

*Distillation gas:*

20.3 cubic meters at 6720 cal./cbm..... 136,200 Cal.

*Water gas;*

From each kilogram fixed carbon 1.8 cubic meters of water gas with a calorific value of 2900 calories per cubic meter are produced. According to the above analysis, 58.0 kilograms of fixed carbon are available; thus

104.0 cubic meters at 2900 calories per cubic meter..... 301,500 Cal.

Distillation gas and water gas together:

124.3 cubic meters representing in heat value..... 437,700 Cal.

so that the calorific value of the gas produced amounts to 3530 calories per cubic meter.

Under operating conditions, however, a certain quantity of distillation gas will be lost while switching the producer from one period to another and also while blowing. For this reason we should expect only about 95 per cent of the theoretical yield of gas. Furthermore we must take into account the fact that not the entire amount of fixed carbon indicated by the analysis is available for gasification because a certain proportion will be left in the slag and escape utilization in the producer. According to analysis, the contents of ash in the coal amount to 10.8 per cent. Assuming that the slag leaving the

producer will contain 10 per cent of combustible matter, in consideration that the coal has a strong inclination for coking and clinkering, there will be only 56.9 kilograms fixed carbon available for gasification per 100 kilograms of coal, instead of the theoretical 58.0 kilograms. Under these conditions 100 kilograms of coal will yield:

95 per cent of the distillation gas:

19.3 cubic meters at 6720 Cal. cubic meters..... 129,500 Cal.

98 per cent of the water gas:

102.0 cubic meters at 2900 Cal. cubic meters..... 296,000 Cal.

all together, 121.3 cubic meters representing..... 425,500 Cal.

from which the calorific value of the gas is calculated to be 3510 calories per cubic meter.

This calculation is based upon the assumption that no tar is decomposed in the process. If the whole amount of tar or part of it is decomposed, the yield of gas as well as the heat produced in the form of gas will be proportionately increased. Also in this direction the probable results of the gasification process can be calculated for individual conditions on the basis of figures gained from experience. As these conditions vary quite considerably in each case according to the composition of the tar and the gasification process itself, it would take up too much time to give details. Also the composition of the gas, which, if no overheating takes place, can be calculated rather accurately will vary under decomposing conditions. Quite a number of practical trials have proved that the yield of gas as well as its composition which had been predetermined by these calculations were actually attained under operating conditions. Of course, a certain although small allowance has always to be made when comparing the theoretically predetermined yield with results obtained on a commercial basis.

In any case the suggested method of determination and the deductions made from it enable us to draw in advance from the results supplied by the chemical analysis reliable conclusions concerning operating conditions. Thus in the predetermination of the gas yield of a fuel by the newly proposed method which consists in a low temperature distillation up to a temperature of 530°C., a subsequent carbonization approaching 1100°C. with a determination of the gas quantity, calorific value and composition of the gas, we have a means to form a conclusive opinion on the conditions guiding the gasification in the producer. Our new method is further characterized by the close

consideration of the single components of the gas as well as the allocation of the heat values to the three phases, solid, liquid and gaseous for coke, tar and gas.

The analysis of gas by testing fuels offers us a series of valuable possibilities which I will discuss here in a general way only; their far-reaching applications, on which I am working in coöperation with my brother Dr. Paul Dolch, will be discussed by the latter elsewhere.

The following train of thought may serve as a basis for all further deductions. Pure carbon burnt in air yields a maximum amount of 21 per cent of carbon dioxide. Upon this fact we can base, as will be shown, quite a number of important conclusions. This proportion will remain constant even if the combustion takes place in steps, as for instance, in the case of gasification and also if the combustion or gasification goes parallel with an introduction of steam. The final result of complete combustion is always and under all conditions the same; in the combustion gases 21 per cent of carbon dioxide and 79 per cent of nitrogen are always present. This is also true for water gas consisting of  $\text{CO} + \text{H}_2$  and  $\text{CO}_2 + 2\text{H}_2$ . With water gas we have to distinguish between two kinds of hydrogen according to their origin: first there is hydrogen which originates from the fuel itself as elementary hydrogen; secondly there is hydrogen which has been formed by the decomposition of water admitted to the producer in the form of steam according to the water gas balances. In order to distinguish both kinds of hydrogen from each other I shall refer to the one originated as apart from the fuel itself as "organic hydrogen" whereas the other, formed by the decomposition of water reacting as vapor upon carbon in accordance with the water gas balance, will be called "inorganic hydrogen." The conception of the maximum contents of carbon dioxide lends us a very important means to distinguish between organic and inorganic hydrogen. That is to say, we are able to calculate in the case of a mixed gas how much of the hydrogen present originates from the fuel itself and what proportion is produced by the water gas reaction. In this connection, however, we have to consider that the gasification of a fuel must be taken as a special case of incomplete combustion and that for the purpose of calculation only the proportion of the fuel should be included which has been actually gasified. The total quantity of combustible matter which was subjected to gasification must be reduced first by the tar, in so far it has not been gasified, and also by those parts of the coke which leave the producer with the slag, having escaped gasification.

Here is an example showing the practical application of these deductions: A water gas, enriched with coal gas from the distillation zone of the producer and which is termed on the European continent "double gas," yielded on combustion 18.6 per cent of carbon dioxide; from this we calculate the respective proportions of organic and inorganic hydrogen at 0.20 and 0.80 respectively. That is to say, 20 per cent of the hydrogen proportion originates from the fuel itself by its distillation and carbonization, while the remaining 80 per cent is due to the water gas reaction. Further conclusions can obviously be drawn from the fact that the method for the distillation of the fuel, which I have already mentioned and suggested, permits a sure determination of the total hydrogen of the fuel as far as it may participate in the gasification without a decomposition of tar. It must be kept in mind that by our method the tar is recovered without decomposition and its contents of hydrogen are thus to be excluded when calculating the hydrogen balance of the process. If thus a larger amount of organic hydrogen has been determined in the gas than was to be expected according to the determination of the gas output, we arrive through our method of testing and calculating at the conclusion that the tar has been decomposed by gasification and from the quantity of organic hydrogen present in excess we can readily form a deduction as to the proportion of tar which has participated in this decomposition.

From the determination of the maximum contents of carbon dioxide we can draw a conclusion as to

1. The amount of steam decomposed in the producer.
2. Whether and to what extent the decomposition of tar has participated in the formation of gas.

We have subjected to our calculation a number of tests, published in England and referring to total gasification in gas producers with high shaft; and we have found that the higher up in the shaft the gas sample is taken, or the greater the distance from the gasification zone, the higher must be the proportion of coal gas developed by distillation in relation to the amounts of water gas produced by gasification, provided the producer is operating normally and no crater has been formed in the fuel bed above the gasification zone. The calculations based upon the maximum contents of carbon dioxide showed in fact that the zones farthest away from the fire bed of the producer yielded a proportion of coal gas developed by distillation which increased in relation to the total quantity of gas, being 9.4, 10.3 and 11.8 per cent

respectively. This method of calculation provides us with easy means to follow up and control the process of gasification and trace all the reactions in a way which previously was not known; and it readily lends itself to a much closer control of the producer and water gas operation than was hitherto possible.

Another important possibility becomes obvious by bringing maximum content of carbon dioxide in relation to the available hydrogen of a fuel.

The proportion of available hydrogen in a fuel relative to its contents of carbon represents—so to speak—the hydrocarbon skeleton of the coal which characterizes the fuel. Between this proportion and the maximum contents of carbon dioxide exists a common relation which enables us to calculate the contents of available hydrogen in the fuel from the maximum contents of carbon dioxide as follows.

The results of the ultimate analysis of the fuel may be given as follows:

Per cent.....	C	H	O	N
Or in atoms.....	$\frac{C}{12}$	$\frac{H}{1}$	$\frac{O}{16}$	$\frac{N}{28}$
The requirements of oxygen for complete combustion equal to.....	$\frac{C}{12}$	$\frac{H}{4}$	$\frac{O}{32}$	— mol O <sub>2</sub>
And to this corresponds by combustion with air and addition of nitrogen equal to.....	3.76 $\frac{C}{12}$	3.76 $\frac{H}{4}$	3.76 $\frac{O}{32}$	$\frac{N}{28}$

From this is calculated:

$$\text{per cent CO}_2 \text{ max} = \frac{100}{4.76 \frac{h'}{C} + 3.76}$$

Where  $h'$  represents the available hydrogen; and further

$$\frac{h'}{C} = \frac{100}{11.28 \text{ CO}_2 \text{ max}} - 0.422$$

Thus we have at our disposal a ready means to calculate from the maximum contents of carbon dioxide the contents of available hydrogen in the fuel. In the beginning of my paper I mentioned that the results derived from the ultimate analysis of fuels cannot be called satisfactory. The possibility indicated by the deduction and calcu-

lation previously shown evidently offers also a means of checking the ultimate analysis of fuels as far as the indirect determination of the oxygen is concerned. In this direction we have carried out a number of trials, aiming at a combustion of the fuel with an excess of air but excluding the usual addition of oxygen from other sources, so that the combustion gases, when tested for carbon dioxide and oxygen, and calculated upon gases free of air, will reflect the proportion of available hydrogen to the maximum contents of carbon dioxide. The result obtained will enable us to calculate the proportion  $\frac{h'}{C}$  and also

TABLE VI

FUELS	VALUE FOR MAXIMUM CARBON DIOXIDE	PROPORTION $\frac{\text{ATOM H}}{\text{ATOM C}}$
Elementary carbon.....	21	0
Solid fuels.....	{ 20 19	0.25 0.54
Liquid fuels.....	{ 18 17 16	0.85 1.19 1.58
Gaseous fuels.....	{ 15 14 13 12 11 10	2.03 2.53 3.12 3.80 4.61 5.58
Hydrogen.....	0	Infinite

the available hydrogen of the fuel. The results of this work which is still under way will be reported later on.

It is not my intention to tire you with all the calculations I have made, but of the many possibilities which offer themselves in following up this train of thought I will mention one somewhat surprising fact. On the basis of these calculations it is easily possible to deduce from the results of the analysis of the waste gases of an internal combustion engine the proportion of  $\frac{h'}{C}$ . From this result we can further draw certain conclusions as to the composition of the motor fuel applied.

I am inclined to believe that the suggested form of calculating on the basis of the composition of the combustion gases will offer quite a number of possibilities which will be adaptable for practical plant operation, although actual trials in this direction have commenced only recently and are by no means concluded.

At last I want to show you a table (Table VI) indicating the relation of the value for maximum dioxide to the proportion between hydrogen and carbon atoms.

Before concluding I wish to make due apologies for having reported at such length, particularly in the latter half of my paper, on experiments and deductions made by my brother Dr. Paul Dolch and myself which are not entirely conclusive. I have done this at the risk of incurring criticism for giving too many suggestions and too few facts because I have felt that this audience, because of the spirit of scientific coöperation which animates it, would not fail to appraise at its true value the motive which caused me to handle my subject in just the manner I have done.

I beg of you to receive my rather incomplete paper, filled as it is with so much that has yet definitely to be established, as a sincere acknowledgment on my part of the obligation I feel to all of you for your open-minded attention and for the warm reception I have found on every hand in your magnificent industry.

#### DISCUSSION

DR. J. C. WARNER (Carnegie Institute of Technology, Pittsburgh): I have been particularly interested in Dr. Noeggerath's paper. I am particularly interested in the fact that under pressure the power consumption is actually somewhat less than under atmospheric pressure. We all know the theoretical voltage for the decomposition of water is bound to increase as the pressure on the gases increases, and we can calculate exactly what that increase in voltage will be.

Here we have a case where in practical operation under very high pressures the power consumption is actually lower than we would calculate. That difference must be due to the fact that some irreversible effects in electrolysis are being decreased as pressures increase. Conductance does increase somewhat with increasing pressure. It may be that at these high pressures, the overvoltage of hydrogen and oxygen is reduced. The increased pressure may also decrease the resistance due to the gas films on the electrodes.

A few points concerning the construction of the apparatus seem to me to need some explanation. I am interested in knowing whether or not any particular type of electrode is used to reduce hydrogen and oxygen overvoltage.

The success of this high pressure cell is undoubtedly closely allied with the success of equalizing pressure on two sides of the diaphragm. I am interested

in knowing how pressure is equalized on two sides of the diaphragm and what sort of a diaphragm is used.

Then the question of the cost of producing hydrogen at these pressures is one that is interesting. From Dr. Noeggerath's tests, made by the German State Railways, I calculate that from 0.086 to 0.1 kilowatt hours are required for a cubic foot of gas. In this country we built ordinary atmospheric cells which are guaranteed to produce a cubic foot of gas for each 0.085 to 0.095 kilowatt hours. These figures correspond closely to the figures given on the test by Dr. Noeggerath.

In this country, in most localities, our hydrogen is cheaper, of course, by the water gas reaction than it is by electrolysis. I understand that according to latest figures, there is a differential pretty close to one-half cent a pound of ammonia between the cost of producing from water gas hydrogen and from electrolytic hydrogen. This comparison is based on electrical energy at 0.3 cent per kilowatt hour.

I do not know how the costs would compare using Dr. Noeggerath's process for producing hydrogen for the fixation of atmospheric nitrogen. In that, of course, we have to keep in mind the pressure required is very high. We use 1000 atmospheres; I think the pressure at which Dr. Noeggerath's cell delivers hydrogen is probably 200 atmospheres.

I am wondering whether the advantage gained by pressure electrolysis will offset the extra cost we have to incur in compressing gas from 200 to 1000 atmospheres. I think the cost of compressing gas is principally in that upper limit.

These are a few things that interested me particularly in Dr. Noeggerath's paper, and they are points on which I would appreciate further information.

The paper by Dr. Stuart was interesting in that it presents some future possibilities. To us in the coal region, the possibility of using water power in this way does not seem so favorable, but in the water power regions undoubtedly an entirely different outlook is had upon the proposition.

CHAIRMAN DIEHL: I have a discussion which has been submitted by Dr. F. J. Clark, Consulting Engineer of Toronto, on the papers of Dr. Noeggerath and Dr. Stuart. I will read the discussion of Dr. Noeggerath's paper first.

DR. F. J. CLARK: *Pressure Electrolysis and its Influence on Fuel and Power.* I have read this paper with more than ordinary interest for the reason that for a number of years I have been investigating the possibilities of pressure electrolysis. Unfortunately my advance copy of this paper does not contain the several figures which doubtless clear up many points of which I am, at present, ignorant.

I have before me, however, the July number of *Chemical and Metallurgical Engineering* and presume that some of the figures are identical. The author presents a very ingenious multiple cell unit for high pressure service, discusses space occupied, gas output and energy consumption but fails to indicate first cost and cell maintenance.

The space occupied relative to gas output is rather better than that of any atmospheric pressure cell now on the market but I will say that if cubical

dimensions rather than floor space are to govern, the described pressure cell has no advantages over an atmospheric pressure cell which can, very shortly, be seen in service.

The current-voltage characteristics, as set forth in *Chemical and Metallurgical Engineering*, do not compare favorably with the atmospheric cells indicated in the paper of Mr. A. T. Stuart.

We have been receiving from time to time for the past five or six years vague hints of revolutionary processes of electrolyzing water at extremely high pressures by the use of apparatus, with and without diaphragms, and I have been called upon to analyze two of these proposals. In both cases there was astonishing ignorance of what was being accomplished in the development of atmospheric cells and in one, not only ignorance of some fundamental physical laws but an endeavor to sell the rights for apparatus that had never been built and would not operate as represented.

I make this comment, not as a reflection upon Dr. Noeggerath for his work in perfecting an operating pressure cell is deserving of great praise which I for one am glad to give. I make it because there appears to be a tendency to underate the progress in the development of atmospheric pressure cells.

With regard to this pressure cell which obviates the need of compressors and using his own tabulated use of energy for gas generation it will be seen that atmospheric cells, operating from 1.75 to 2.25 volts through the range of current used, will with the same expenditure of energy for compression as noted on the charts, require from 20 per cent to 30 per cent less energy than the pressure cell described.

Before this pressure cell can be seriously considered for the many uses suggested, the author will have to deal with the economics of capital costs, operating, maintenance and other expenses which are not mentioned in the paper.

In this connection and also with regard to the fundamentals of his process he will have to deal with temperature which has an important bearing upon every one of the essential factors mentioned, and which purposely or otherwise has been omitted from the discussion although indicated on the diagrams.

It is apparent that Dr. Noeggerath claims apparatus having inherent superiority over whatever may be possible with atmospheric apparatus and assumes that high pressure is an essential. I could array many arguments to demonstrate that for many uses of the gases, particularly where very large installations are involved, the high pressure may be of no value or a possible detriment.

It is necessary to have the relation of temperature to the current-voltage characteristics of this high pressure cell before it can be suitably compared with atmospheric cells. It would be futile to speculate upon the future possibilities without knowledge of capital costs and maintenance charges.

If Dr. Noeggerath will supply these needs there will be an opportunity for those interested to arrive at a conclusion as to the industrial merits of this apparatus.

CHAIRMAN DIEHL. In that same connection, Mr. Clark has also submitted a discussion on the paper of Mr. Stuart.

DR. CLARK: *Some Potential Relations Between Electricity and Coal Utilization.* This paper is a very valuable contribution to this conference.

The relation of electric energy to the processing of coal has been presented in a most logical manner.

The author impressively demonstrates the relation of water to coal for the production of the more valuable attainments of coal processing, and I want it to be understood that I am in hearty agreement with the entire presentation as to the relation of oxygen and hydrogen to coal processes.

Such criticisms as I shall make are to be understood as intended to be constructive and relate in general to a somewhat different reaction to the economies of this presentation than that to be taken from this paper.

Relative to the last paragraph of III a doubt remains regarding the possibility of using all the oxygen in coal processing. As heating gas is one of the important products and as oxygen can always be used to convert coke and carbon dioxide to carbon monoxide there should be no surplus oxygen where combustion is a part of the subordinate processes. The author deals with this in IV but fails to bring out this possibility.

In V the author appears to premise his conclusions upon cells to operate at 1.75 V and compares these cells with what, for want of a better explanation, must be taken as present practice at 2.75.

If we disregard fixed charges and maintenance the conclusions reached are unimpeachable but those who supply the capital for these new undertakings are hardly likely to do so.

Purchasers of electrolytic cells will base their selection on the cost of the gases or of the one gas needed and for a period of years during which the largest item of expense electrical energy, remains constant.

The author has firmly established that an efficiency of current use expressed as one volt per cell produces a saving of about 36 per cent in energy under the conditions given. For a 10,000 ampere cell the annual use of energy would be—

$$\begin{aligned} 10,000 \text{ amperes @ } 2.75 \text{ V for 8760 hours} &= 240,900 \text{ k.w.h.} \\ 10,000 \text{ amperes @ } 1.75 \text{ V for 8760 hours} &= 153,300 \text{ k.w.h.} \\ &\underline{87,600} \end{aligned}$$

*Saving—*

$$\begin{aligned} 87,600 \text{ k.w.h. @ } \$ .001 &= \$87.60 \\ 87,600 \text{ k.w.h. @ } .002 &= 175.20 \\ 87,600 \text{ k.w.h. @ } .003 &= 262.80 \\ 87,600 \text{ k.w.h. @ } .004 &= 350.40 \end{aligned}$$

If we assume that operation and maintenance costs are not very different for the two voltages and attempt to determine how much more can be spent to attain 1.75 volt operation we must know the annual rate for fixed charges, as well as the cost of energy.

With energy at \$.001 per kilowatt hour and fixed charges at 10 per cent it is \$876 per cell, or with fixed charges at 20 per cent it is \$438 per cell.

With energy at \$.003 per kilowatt hour, which is probably a very high rate for any large cell possibility, when fixed charges are 10 per cent the cell cost can be increased \$1752 or with the charges at 20 per cent it is \$876.

It must be borne in mind that the author makes much of the use of these cells to absorb off-peak energy as and when available. This means something less than 100 per cent use of the apparatus, and if the average use of the cell apparatus is 50 per cent then the effect is the same as doubling the fixed charges.

Now although I am in general agreement with the author I fear the effect of attempts on the part of engineers to substantiate the extremely low costs pictured. In my opinion these costs may be future possibilities but they are, for several reasons, not at present attainable, nor are they necessary to promoting a very great use of electrolytic apparatus.

I specifically question the advisability of using 1.75 volt cells because of their cost and a strong conviction that their maintenance expense will be heavy.

I cannot escape the conviction that the author is painting a picture rather than adhering to the facts in suggesting that 2.75 or even 2.5 volts is the existing practice in water electrolysis. Some cells may equal or slightly exceed 2.5 volts for short periods but 2 volts to 2.3 volts is more nearly existing practice. For these low voltages the chlorine corrosion explanation will not answer. Oxygen and its physical state is much more likely to explain corrosion and it is not unlikely that the process of electrolysis, which varies with the types of cells, will alter the effects of corrosion.

The author's suggestion that the lowering of the voltage from 2.75 to 1.75 "practically eliminates the otherwise high costs in up-keep repairs and amortization" will be relatively important when proved. In so far as this discussion is concerned it will be generally doubted and there will attach to it only such confidence as will rest in an unproved statement.

The author's suggestion that large power plants equipped with 100,000 h.p. of water wheel or steam turbine driven D.C. Generators will be built is possible but hardly probable and he apparently assumes that the D.C. apparatus will cost no more than A.C. apparatus. It might, therefore, be a surprise to learn that in a number of cases actually estimated it was cheaper to install large A.C. generators and get the D.C. current from rotary converters.

In VII the author suggests that the costs, exclusive of energy, will not exceed 5 cents per 1,000 cubic feet of hydrogen, and as this is about half the lowest cost I have ever been able to approximate it will be challenged as leading to an expectancy which cannot be realized. If the author has meant to exclude fixed charges then I will be in agreement.

The author's suggestion that power companies may be induced to operate their plants without profit, no matter what the output is to be used for, is unfortunate and will tend to detract from the many other suggestions of value in this paper.

There is no such thing as electric energy at no cost and still less of a possibility that it can be purchased or used on any such basis. I believe that when electric energy is to be had in industrial localities at low rates such as 1.5 to 2.5 mills per kilowatt hour the energy will be off-peak intermittent power available at from 40 to 60 per cent average capacity use.

Extra plant expense will be necessary for this and it is possible that if hydrogen is to bear the cost, the hydrogen may be had at about 30 cents per 1,000 cubic feet when A.C. energy costs 1.5 mills per kilowatt hour.

Finally, I reiterate that these criticisms are intended to aid rather than detract from this paper which is a very important addition to the subject matter of coal and its uses.

MR. STUART: Mr. Clark questions the advisability of using 1.75 volt cells because of their cost. However, it should be pointed out that most apparatus in use ceases to function at all at such voltage and that, therefore, it is not logical to generalize. Whether or not it is economically feasible to operate at 1.75 volts will depend of course, upon the characteristics of any particular cell in question. In referring to such voltage, the writer is quoting from his own experience in the design and operation of cells.

Mr. Clark states that gas costs of 5 cents per 1,000 cubic feet, exclusive of energy, cannot be realized. This generalization also can be questioned when it can be pointed out that a 10,000 ampere cell is capable of producing per year 2,100,000 cubic feet of gases. The estimate of 5 cents per thousand, therefore, provides \$105.00 per year per cell to cover all costs of operation other than power. If such costs are estimated at 15 per cent then a capital cost per cell of \$700 can be carried or, if estimated at 20 per cent, a capital cost of \$525 can be carried. There is therefore no good reason for stating that costs must exceed 5 cents per thousand cubic feet of gas.

CHAIRMAN DIEHL: The papers are now open for any further discussion.

DR. WARNER: One more thing has occurred to me in Dr. Noeggerath's paper. The critical voltage was about 2.5 volts. I am wondering whether this critical voltage is in any way determined by the distance between the electrodes; whether the critical voltage will vary with the distance between electrodes.

DR. NOEGGERATH: In connection with the question Professor Warner asks, the critical voltage depends upon the distance between the electrodes and many other factors. The deciding factor, as I said in the paper, is the specific quantity of gas produced. Specific quantity means in relation to the sections and many other relations to the cell.

As to the cost of compression to high pressures, up to 1000 atmospheres, I think these plants are 150 and 200 atmospheres because that is the pressure usually used for commercial purposes in Europe. Of course, nowadays with the process the pressures go up much higher.

There is no reason why it is not possible to go higher with the pressure on the pressure-electrolyzer. Also, the first stage of compression is done with the pressure-electrolyzer, and the higher stages are reached by compressors. Just before I left Europe I was told it was an advantage to have the lowest stages of the compressors, not the highest, eliminated because the lower stages are those of the large volume cylinders and the saving is more than with the higher stages.

I do not know whether I answered all the questions of Professor Warner.

As to Mr. Clark's remarks, he very rightly said that in comparing the values of various electrolyzers, it is absolutely necessary to know the temperatures.

The paper he had before him was the reprint appearing in the July number of *Chemical and Metallurgical Engineering*. That was only a short abstract of the paper I read in Berlin. It is possible that the temperatures there were not given. In this paper they are given. All the figures I gave referred to 20°C. for the gases, and referred to a very low temperature of the electrolyte, namely, 35°. With increasing temperature of the electrolyte, the efficiency, of course, is higher. I operated these series at about 55°, which is lower than the average temperature, and obtained the good results shown.

He further said that the value of the curves did not compare favorably with those he knows of. There again, there is a difference between my Berlin paper and the paper I presented here. There the average consumption lies between 3 and 3.5 kilowatt hours per cubic meter of gas. On the other hand, the curves in the paper are much higher. He did not mention the fact that I was using 3 to 3.5 kilowatt hours per cubic meter of gas, but referred to the curves.

The reason why the curves show higher values is that these curves show overload conditions. Everybody knows that with an increase of current density, the voltage rises. These curves were given because they showed more clearly the effect of the pressure upon voltage and so forth, as it is given at lower loads. These curves, I think, showed three or five times the normal load. It is of particular advantage to the electrolyzer. You can operate with very great overloads while in an ordinary cell the gases produced will carry off the electrolyte.

The figures for kilowatt consumption are 3 to 3.5 per cubic foot of gas. This is not a fixed kilowatt consumption; it is simply a kilowatt consumption which for European conditions proved to be an acceptable and a very good one. Of course, it is possible to reduce the kilowatt consumption by operating the cell at a lower current density, making the cell a little more expensive. I found with the conditions existing in Europe I could meet all conditions. I will give you an example. Shortly before I left Europe there was a request for a rather large plant for the fixation of nitrogen. I put in a bill for that and the capital cost was approximately 30 per cent lower than that of the lowest competitor, although the prices on the atmospheric electrolyzer had been cut down appreciably. In addition, the yearly saving was considerable, although I had put in a yearly royalty fee. So it is proven that the cost is very much cheaper. If you want any more details I will be glad to give them to you.

To give you actual figures as to the cost of the cell would not mean much because I do not know the manufacturing expenses as they would exist in America. I could not tell you what a cell of mine would cost if manufactured in the States. That, of course, is also a question not only of material but it is a question of the manufacturing organization. If the cells are manufactured in very large quantities they could be manufactured much more cheaply than in Europe, but otherwise they would probably be much more expensive.

As to the first cost, that is another very important item. The cost of the electrolyte usually amounts to quite a considerable figure, but these cells are so small that the amount of electrolyte used is approximately three gallons per 35 cubic feet, that is, about one gallon to 12 cubic feet. That amount is so small that it is of practically no account compared with the cost of the cell.

As to the maintenance, no electrolyte is lost, and as far as my experience goes during the last two and one-half years, the maintenance cost must be very small because during this time there was no sign whatsoever of a change in the electrodes or in the diaphragm. The electrodes are of iron, nickel-plated. I have very recently made further improvement, by which I was able to increase the current density by 60 per cent without increasing voltage.

DR. WARNER: Can you tell us something about the pressure equalizer?

DR. NOEGGERATH. I can only answer that in a negative way because of the patent situation. I will say this much; the pressure equalizer does not require any levels or any electric connections, or any gauges of any kind, but just how it is done, in the simple way I do it, I unfortunately am not able to disclose at this moment. I think I said in the paper that I put it up to 300 atmospheres on one side of the cell and the gauges showed equal pressure on both sides.

F. ZUR NEDDEN (Federal Coal Council, Berlin, Germany): There is one point in the discussion which I am not sure whether the gentleman who presented the written discussion has taken into account. That is the space and the building connected with a compressing plant. Artificial compression ought to be more expensive than compression within this apparatus. Mr. Warner gave some figures from which it appeared that the current required for atmospheric electrolysis is about the same as the current required for electrolysis at 200 atmospheres, which Dr. Noeggerath mentioned. If the current is the same I really do not know why there should be any extra charge for compressing. Mentioning the current alone, I do not know why there should not be an extra charge for the capital and the maintenance of the compressor which is necessary for compression.

I really cannot see why it should be possible to compress atmospheric hydrogen and yet come down to the figure which was named by Dr. Noeggerath.

Furthermore, the discussion does seem to me to have completely forgotten the fact that the hydrogen which is generated at high pressure in Dr. Noeggerath's apparatus is absolutely, or as nearly absolutely pure as possible. The hydrogen generated from coke oven gas would have to undergo a purification treatment. Of course, the cost of that purification treatment is usually forgotten, but it should be put in. Probably the calculation would then be again in favor of the high pressure electrolysis.

I am of the opinion that all these factors should be very carefully kept before you, otherwise, we will arrive at wrong and hasty conclusions.

I might add the mere fact that Dr. Noeggerath has been able to put a plant in at the German State Railways is about the best recommendation he could possibly have, because if any people on earth are hard to get at it is the German State Railways.

DR. NOEGGERATH: As to the cost of production and the kilowatt hours required to manufacture cubic meter gas, and the remarks that were made comparing my figures with that of an atmospheric cell, the men who asked

these questions all forgot to add that they also have to compress afterwards in most cases, and in some cases up to 1000 atmospheres. It is all right to compare an atmospheric electrolysis with another one by giving the voltage of 2.3 volts, but in addition to that you have to add the compression energy of the compressor, which in large plants may go down to below 0.5 kilowatt hour per cubic meter, and in small plants go up to much higher figures than that. So you cannot compare the voltage. I keep within the voltage of 2 or 2.3 volts.

As far as the cost of maintenance is concerned, of course that comes in in a rather not too small value.

## SOME ASPECTS OF THE HYDROGENATION OF COAL

By J. IVON GRAHAM

*Assistant Director, Mining Research Laboratory, University of  
Birmingham*

On the occasion of the last Bituminous Coal Conference held in Pittsburgh in 1926, the pioneer of this method of coal treatment, Dr. Friedrich Bergius, gave some interesting details of the large amount of research work carried out by himself and his coworkers. Some idea of the enormous cost of the researches carried out by the Erdol and Kohlenverwertung A. G. during the past fifteen years has also been given recently by Herr Bruchmanin, the president. He stated that during this period the cost of the investigations had amounted to about 28 million gold marks—a figure which will not appear exaggerated to anyone who has visited, and admired the organization of, the works at Mannheim. The investigations of the I. G. Farben Industrie groups combined with those of the Bergius syndicate has resulted in the erection of a large plant at Leuna which, it is stated, is capable of an annual output of over 100,000 tons of oil from the treatment of brown coal. How far this particular commercial plant has been a success, it is probably too early to judge.

It is not, however, upon the economic side of the problem that I wish to dwell but rather to discuss the influence of composition of coal upon the quantity and nature of the compounds produced during the action of hydrogen at high pressure, upon coal at a temperature in the neighborhood of 430°C.

The possibility of the conversion of coal into oil has now been proved by various investigators in different countries. In 1923 researches on the high pressure hydrogenation of coal were commenced in the Mining Research Laboratory, Birmingham University, under my supervision and with the approval of the Director, Dr. J. S. Haldane, C.H., and as a result of the practical interest shown by Sir John Cadman, K.C.M.G. Since 1924 the work has been continued with financial aid from the British Colliery Owners' Research Association. Our aim has been to investigate the question of the hydrogenation of coal in a somewhat less empirical manner than appears to have been the case in the researches of Bergius and other investigators. Thus by studying the action of hydrogen upon the

macroscopic constituents of coal, namely, durain, clarain, vitrain and fusain, and also the  $\alpha$ ,  $\beta$  and  $\gamma$  compounds, into which coal may be separated by the successive solvent action of pyridine and chloroform, we have endeavored, and are continuing our endeavors, to learn more about those constituents of coal which are most readily attacked by hydrogen. After experiments upon one or two different coals, the advisability of a more complete investigation of the action of hydrogen upon British coals became apparent in order to learn the influence of type and composition upon oil yield.

During the years 1923–1924 the tests were for the most part carried out by Mr. H. G. Shatwell, while since 1924 Mr. D. G. Skinner has been responsible for the greater portion of the experimental work in this section of our researches. Some of the results have been published in papers by these gentlemen and myself in *Fuel in Science and Practice*<sup>1</sup> and elsewhere.<sup>2</sup> The action of hydrogen upon coke prepared from lignite has also been investigated, while more recently considerable attention has been paid to the action of catalysts. The influence of various factors such as fine grinding, temperature, and pressure have also been investigated. In practically every case the products of the reaction, solid, liquid and gaseous have been analyzed.

In his early patents Bergius drew a somewhat artificial line of demarcation between coals containing less than 85 per cent of carbon (on an ash-free dry basis) and those containing more than this amount. The former were considered to be capable of ready and almost complete conversion into a tar-oil whereas of the latter only a certain proportion could be liquefied. Working upon this statement of Bergius we started our investigations with a non-coking bituminous coal of high oxygen content from the South Staffordshire Thick Coal. This was separated into durain, and clarain, with each of which was associated a small amount of vitrain. Preliminary experiments showed clearly that hydrogenation of the dried dust at 420°C. and 124 atmospheres did not yield any considerable amount of oil. Nevertheless an interesting insight into the primary reaction between hydrogen and clarain was obtained. A hard lustrous coke was formed, a similar substance being produced by treatment at the same temperature in nitrogen under pressure. The analyses of the two products were, however, very different, that from the hydrogen

<sup>1</sup> Fuel, 1925, pp. 25–30, 75–80, 127–130, 474–485; 1927, pp. 74–81.

<sup>2</sup> Trans. Inst. Min. Eng., lxx, 2, pp. 86–106; Inst. of Fuel, 1927.

treatment possessing C 90.58, H 4.34, O 3.01, while the nitrogen product had C 85.42, H 4.63, O 8.03. The volatile matter in the hydrogen product was 18.63 per cent and chloroform extract 3.98 against a volatile matter of 24.48 per cent and chloroform extract of 2.48. The results showed that the initial reaction is one of removal of oxygen and, in the case of the clarain experimented with, this oxygen is largely present in the form of hydroxyl groups. These groups are partly removed by heating in nitrogen, i.e., by ordinary distillation, but more completely by treatment with hydrogen. Other experiments were carried out with the coal in the dry state

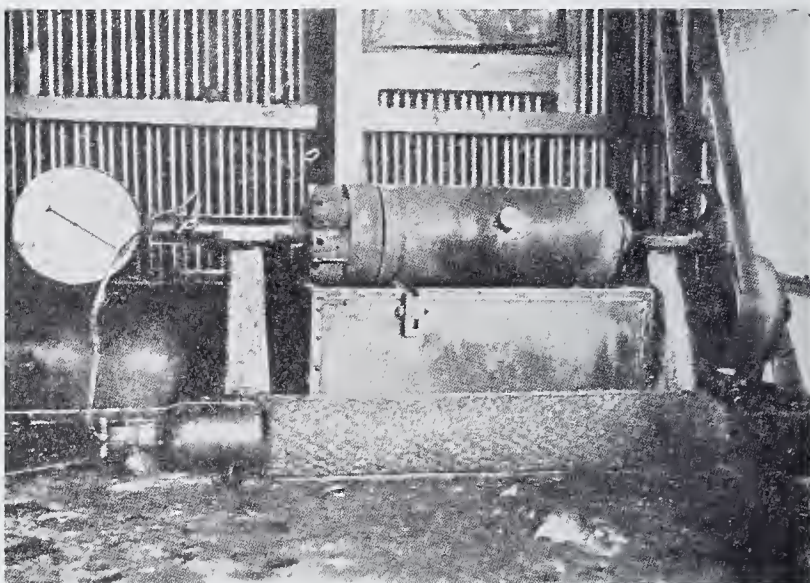


FIG. 1. HIGH PRESSURE AUTOCLAVE

but without success so far as appreciable oil yield was concerned. It was then decided to follow the lines adopted by Bergius and use a coal mixed with gas oil (previously hydrogenated). This experiment resulted in a considerable production of oil. As, however, the products were difficult to separate from the gas oil we decided to use a suspending medium which would not be affected by the experimental conditions but which could be readily removed from the coal and products. Phenol was found to be unattacked under our experimental conditions and as this compound is readily removed by treatment with caustic soda we decided to employ it as a suspending medium for the coal. Obviously there is a considerable drawback

to the use of this material, in that any phenols produced during the reaction will be lost. However, it has been shown that the amount of such compounds produced is small and the advantages of the use of phenol were therefore considered sufficient to outweigh this source of error.

Although the experimental details have been described in previous papers in England, it may not be out of place to mention briefly the procedure adopted. The three-liter autoclave shown in Figures 1 and 2 has been used for the majority of the experiments. It is composed of steel containing 3 per cent nickel and 0.5 per cent carbon and the minimum thickness of the wall is 3 inches. The autoclave is heated

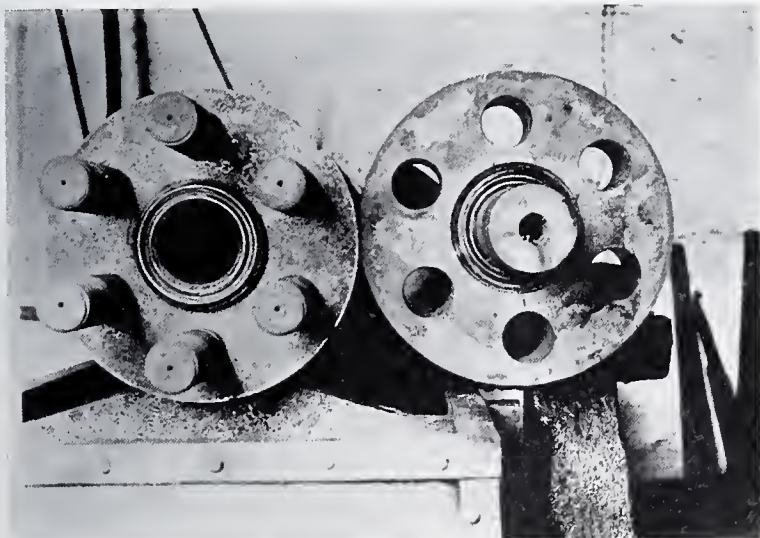


FIG. 2. HIGH PRESSURE AUTOCLAVE—SHOWING JOINT

by gas and is rotated during an experiment to prevent superheating of the charge (and consequent coking). The temperature inside the autoclave is obtained by means of a mercury-in-steel distance thermometer, the bulb of which fits into a pocket which passes through the shaft on the right-hand side of the picture and reaches into the center of the autoclave. The autoclave is closed by means of a cover which forms part of the shafting (shown on the left-hand side of Figure 1). This cover is kept in position by six  $1\frac{1}{2}$ -inch bolts, the pressure joint being produced by a W projection on the autoclave fitting into a soft copper washer carried in the cover. The autoclave and cover are shown "end on" in Figure 2. The cover and shafting

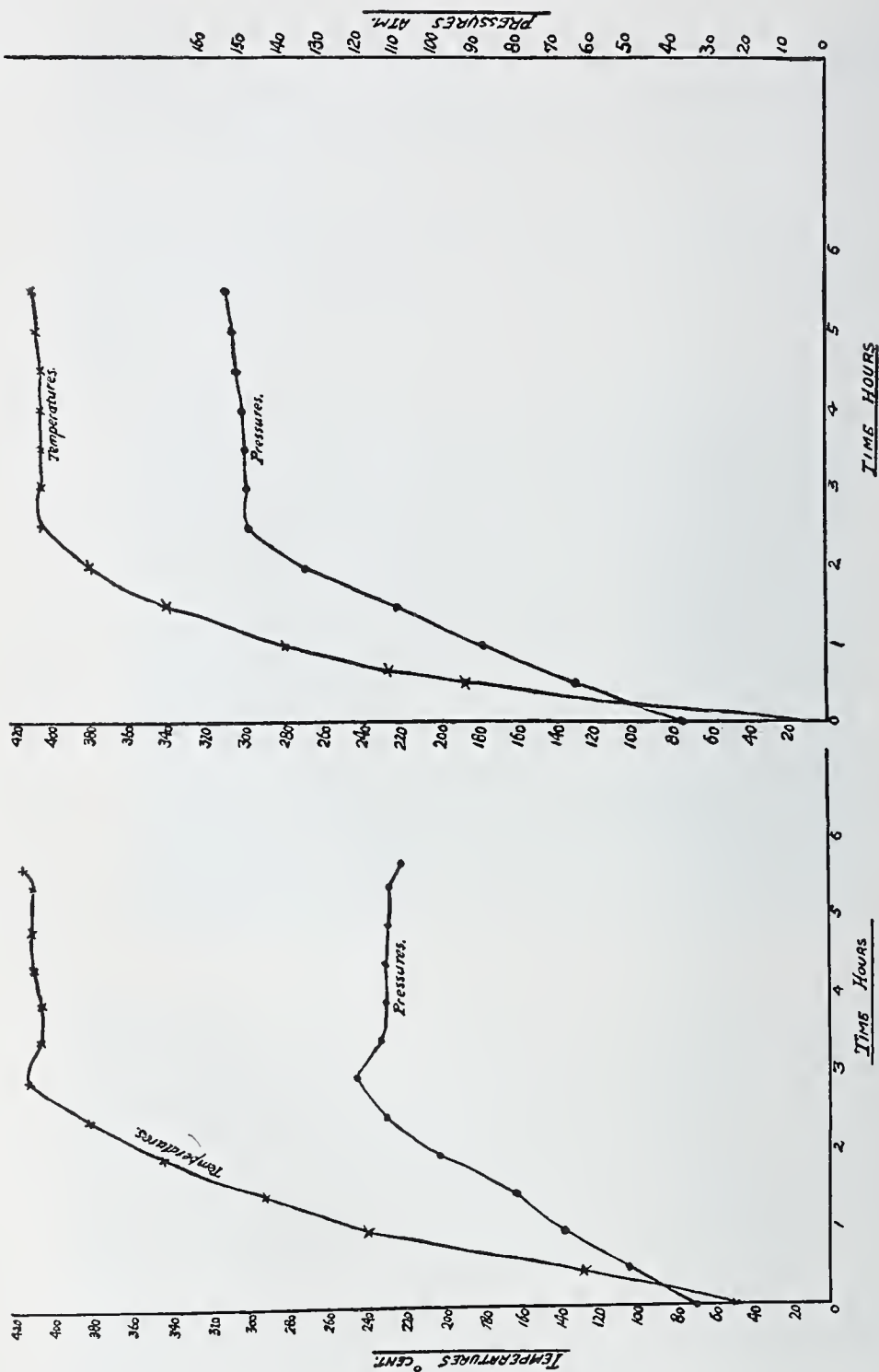


FIG. 3

FIG. 4

have a  $\frac{3}{4}$ -inch bore connecting the autoclave with the pressure gauge and the valve through which gas can be admitted or discharged. A plug screwed into the autoclave facilitates the removal of the liquid products.

In some of the earlier experiments the proportion of coal to phenol was 1:2. It was felt that for comparative purposes the proportion used by Bergius should be followed and therefore in all tests since 1925 200 grams of coal have been mixed with 100 grams of phenol. The use of the smaller quantity of phenol was found to have no appreciable effect upon the oil yield but facilitated appreciably the subsequent filtration. For the comparison of the behavior of various types of coal the experimental conditions of hydrogenation were kept so far as possible the same. In each test the mixture of 200 grams of coal with 100 grams of phenol was placed in the autoclave and, the latter having been sealed, hydrogen was admitted in every case until as nearly as possible the same pressure was obtained.

Some of the early experiments showed that the greatest amount of hydrogen absorption took place during the first four hours and that the difference in yield between a 12-hour test (in which a fresh supply of hydrogen was added after 4 and 8 hours respectively) and one of 8 hours was small. It was therefore decided to adopt a standard of eight hours for the time of treatment of the coal at 430°C.—this period being divided into two periods of four hours each, the autoclave treatment being spread over two days. The time taken to heat the autoclave up to this temperature was usually about two hours and at the end of the four hour period the heating gas was shut off and the autoclave allowed to stand until the following day when the pressure was noted and the cold gases blown off into a gas holder, measured and a sample taken for analysis. The autoclave was then charged with fresh hydrogen and the heating process carried out for a further four hours and controlled to give a temperature of about 430°C. On standing over night the pressure was again noted and the residual gases measured and sample taken for analysis.

Figures 3 and 4 illustrate the way in which the pressure followed the temperature rise in two experiments carried out in 1923 by Shatwell on clarain from the South Staffordshire thick coal. In the first case hydrogen was used in the autoclave and in the second nitrogen. The shape of the pressure curve in Figure 3 (hydrogen) indicates clearly that the absorption of hydrogen became rapid when

a temperature of 412°C. was reached. No such absorption has occurred in the case of the nitrogen experiment. On cooling, the pressure in the hydrogen experiment was found to be 23 atmospheres against 35 atmospheres at commencement, whereas the final pressure in the case of the nitrogen experiment was 41 atmospheres, this being an increase of 3 atmospheres over the starting pressure (cold).

The gases having been blown off, the general procedure has been to remove the solid and liquid products of the reaction and to heat these in a Fischer retort up to 150°C. for the purpose of collecting the light fraction, (D) and water. The light fraction was in each case separated from the water, washed with dilute caustic soda (to remove phenol), dilute acid and finally water. The residue in the retort was then filtered from the phenol and tar oil, washed with further quantity of the former to remove as much as possible of the oil and then treated with caustic soda solution, water and finally dried in vacuo. The phenol soluble portion was next treated with caustic soda solution and the oil and precipitate formed further separated by extraction with chloroform. The products obtained in this way were as follows:

- A. Residue insoluble in phenol—black solid.
- B. Portion soluble in phenol insoluble in chloroform—brown powder.
- C. Portion soluble in phenol and in chloroform—tar-oil.
- D. Light spirit boiling below 150°C.
- E. Water.
- F. Gases.

A separation on these lines gives rather more information than can be obtained by simple distillation of the products of the reaction.

Table I summarizes the results of the experiments carried out in our laboratory and compares the yields of coke, oil, etc., from hydrogenation with those obtained by destructive distillation as carried out in the Gray-King Assay apparatus on a 20 gram sample of the coal.

In the first place it will be seen that in the case of most coals there is a very marked increase in the oil produced under hydrogenation conditions over that formed by distillation. Certain of the claims of Dr. Bergius are therefore supported by the results of our investigations. A very considerable difference is shown between coals of different type, and by reference to Table II it will be seen that when arranged according to Seyler's classification, the type of coal which

is most amenable to hydrogenation under the conditions of our test is the Parabittuminous. Sample 23 appears to be an exception but the low oil yield has, most probably, been due to the coking which

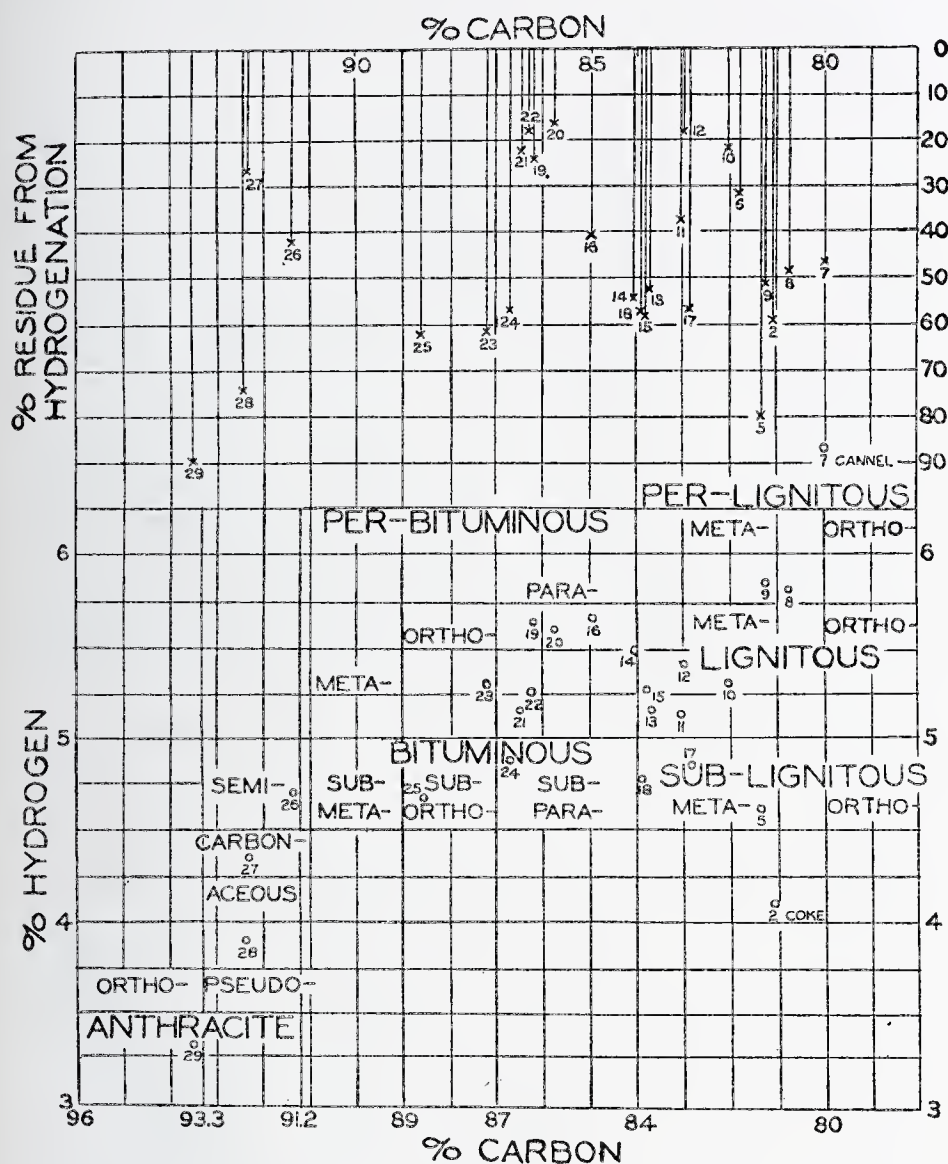


FIG. 5. SHOWING POSITION OF COALS IN SEYLER'S CLASSIFICATION

was found upon opening the autoclave, to have taken place. Certain coals in other positions in the classification have, however, also given a comparatively high yield of oil and a small residue. One of these

TABLE I  
COMPARISON OF THE RESULTS OF HYDROGENATION WITH THOSE OF DESTRUCTIVE DISTILLATION  
(All results expressed as a percentage of ash-free dry coal)

	PRODUCTS OF DESTRUCTIVE DISTILLATION AT 450°C.				HYDROGENATION AT 430°C.					
	Coke residue	Tar oil	Water	Total gas	A Residue insoluble in phenol	B Soluble in phenol and in CHCl <sub>3</sub>	C Tar-oil soluble in phenol and in CHCl <sub>3</sub>	D Light spirit	E Water	F Total gas
1.* Lignite Devon.....	52.7	11.45	6.8	15.8	20.3	20.3	40.3	—	—	16.1
2.* Lignite, Devon, coke at 430°C.....	—	—	—	—	59.6	10.9	24.2	—	—	20.2
3.* Brown Coal, Cologne.....	61.6	14.05	5.0	16.0	24.9	17.4	39.7	—	—	11.1
4.* Recent Lignite, Devon.....	57.2	23.8	9.45	10.2	16.3	3.6	29.3	—	—	11.4
5.* Recent Lignite, Devon, coke at 430°C.....	—	—	—	—	79.3	2.9	6.1	—	—	1.3
6.* Boghead Cannel, Fifeshire.....	39.2	48.4	1.95	7.0	31.9	nil	48.4	3.21	4.8	12.6
7.* Cannel Coal, South Staffs, Thick Coal.....	63.4	22.95	6.55	5.55	46.3	1.9	28.1	6.82	—	13.8
8. Vitrain, Slate Seam, Warwickshire.....	78.0	10.2	5.9	5.55	48.8	2.6	17.4	4.3	9.6	13.8
9. Ell Spires, Warwickshire.....	73.4	13.5	3.25	6.55	51.9	4.6	18.8	5.3	6.1	8.2
* South Staffs, Thick Coal, White Seam:										
10. Clarain.....	—	—	—	—	21.8	6.0†	37.7†	—	—	13.1
11. Durain.....	73.7	8.95	11.05	5.8	37.5	7.5†	37.5†	—	—	6.7
12. No. 1 Seam, Somerset.....	82.8	11.40	1.35	4.15	18.4	18.3	33.9	—	—	19.7
13. High Hazels, South Yorks.....	75.6	14.3	3.95	5.25	52.6	2.7	16.7	4.7	7.7	14.7
14. Namdang, India.....	74.0	17.2	1.6	4.8	54.1	1.2	14.4	6.3	8.4	16.4
15. Barnsley Softs, South Yorks.....	77.1	13.1	3.5	4.4	58.0	1.1	15.8	6.3	8.4	12.1
16. High Delf, Gloucestershire.....	84.7	11.95	0.75	2.6	41.0	5.4	31.2	5.2	7.3	9.8
17. Nottingham Top Hard, Soft Coal.....	74.0	5.5	6.55	6.35	56.8	3.8	18.2	4.0	5.4	14.0
18. Nottingham Top Hard, Hard Coal.....	83.7	10.1	2.8	3.3	57.6	1.1	16.3	6.0	8.4	11.4
19. Bullhurst Tops, North Staffs.....	84.3	10.8	1.0	1.55	24.5	9.4	38.0	7.0	7.6	14.6
20. Arley, Lancs.....	82.0	12.7	4.6	—	16.4	6.2†	61.4†	—	—	8.9

21. Wing Vein, South Wales.....	83.7	9.65	3.35	4.4	22.6	14.5	52.3	—	—	15.2
22. Seam A, North Staffs.....	77.0	12.35	4.1	6.3	18.2	10.3	43.7	8.3	4.0	17.0
23. South Fawr, South Wales.....	84.8	9.5	1.15	3.65	62.2	1.4	14.8	3.8	5.4	15.6
24. Five Feet, Fifeshire.....	82.9	8.85	1.8	4.8	56.9	5.3	16.9	4.2	6.5	12.3
25. Seam A, South Wales.....	92.5	3.7	0.2	2.0	62.9	6.6	17.9	2.1	4.5	8.0
26. Seam A, Kent.....	96.4	1.65	0.05	1.35	42.3	6.7	31.1	4.4	5.1	12.3
27.* Graigola, South Wales.....	93.4	2.6	—	—	26.5	33.1†	26.1†	—	—	2.0
28. Hughes Vein, South Wales.....	98.7	0.20	0.2	1.0	74.3	4.7	9.7	1.6	4.0	13.8
29. Big Vein, South Wales.....	98.3	0.05	0.6	1.25	90.53	0.59	1.56	1.07	4.8	2.1

\* Hydrogenaton carried out using coal: phenol in proportion 1:2.

Time of hydrogenation:

No. 1.....	hours
No. 2.....	12
No. 10.....	8½
No. 11.....	13
No. 20.....	16
No. 27.....	12
Remainder of samples.....	9
	8

† Ether used in place of chloroform for separation of B and C in these experiments.



we were particularly interested to find was No. 27, a Welsh steam coal (slightly coking)—which is of high carbon content and belongs to the carbonaceous genus. Again Nos. 10 and 12 among the metaliginitous coals gave a higher yield than others in the same group.

Figure 5 gives a diagrammatic representation of the samples used showing their position in Seyler's classification and also of the amount of residue left after hydrogenation under our standardized conditions. From this, the position occupied in the classification by those coals which appear to be most amenable to hydrogen treatment can be seen more readily, and it is clear that the early view of Bergius in regard to the carbon content of those coals easily liquefied (namely, those containing less than 85 per cent on an ash-free dry basis) is not supported by our work. It may be argued that the pressures employed by us have not been so high as those used by Bergius and other workers. Experiments carried out by D. G. Skinner using hydrogen pressures up to 245 atmospheres have, however, shown that the consequent additional conversion of solid residue into liquid products is not very marked. The influence of increase in temperature from an average of 430°C. to one of 457° and a maximum of 473°C. was tested in the case of sample No. 29 and only reduced the residual solid matter 3 per cent.

The table includes the results obtained in some of the earlier tests in which the heating was carried on, in some cases for twelve or more hours. Thus sample 20, tested by Shatwell and Bowen, was treated for twelve hours. Very little further absorption of hydrogen occurred, however, after the sixth hour. The sample of the South Staffordshire clarain, although heated for thirteen hours in four successive periods, absorbed the major portion of the hydrogen during the first five hours. The comparison of these coals, as set out in the tables, is therefore, I think, quite justified and the results will, in my opinion, give a good indication of what may be expected in the way of conversion, when the operation is carried out on a larger scale.

Values for light spirit and water are missing in the earlier experiments as in these cases the preliminary distillation up to 150°C. of the mixed products from the retort was not carried out.

It will be noted that the quantity of product B varies considerably, but, generally speaking, where the greatest amount of action has taken place, i.e., where the residue (A) is small, the largest amount of product B is found. In some of the earlier experiments ether was

used in place of chloroform—but subsequent tests have shown that the action of the latter is practically the same as that of ether. That B is a definite hydrogenation product has been proved by numerous “blank” experiments on the different coals using nitrogen in place of hydrogen. Only a fraction of a per cent of portion soluble in phenol and insoluble in chloroform has been found to be formed under these circumstances. How far B can be further hydrogenated, if at all, is the subject of further investigation. Product C is the tar-oil and combined with D the most important product from the commercial point of view. In the tests carried out at Birmingham, C has been redistilled and separated into fractions boiling below 300°C. and between 300° and 450°C. The former fraction has, in most cases, amounted to approximately 25 to 35 per cent of the product, except in four or five cases when about 15 per cent of the product distilled below 300°C., while in nearly all cases between 30 and 45 per cent boiled between 300 to 450°C. The iodine value of the distillate below 150°C. was found with one or two exceptions to be between 120 and 150 (Wijs) whilst that of the fraction distilling below 300 varied between 94 and 358. The products were thus moderately well saturated and differ in this respect from similar fractions formed by destructive distillation or in the “blank” tests carried out in nitrogen when an iodine value of the order of 500 to 600 was found.

The water produced in the autoclave is no doubt partly the result of distillation and partly of hydrogenation. The total production of water follows more or less the oxygen percentage of the coal. If one takes the difference between the value, E, and that for the water produced by destructive distillation figures are obtained which should show the water produced as a result of the action of hydrogen. The amount produced is, in most cases, between 4 and 6 per cent of the ash-free dry coal. There does not appear to be any marked connection between this yield and the content of oxygen, or of any other single element in the coal. The fact that more water has been formed in the case of No. 29 than could be produced if all the oxygen in the coal were transformed, casts a certain amount of doubt upon the absolute accuracy of the moisture figures.

Turning now to the gaseous products of hydrogenation it will be seen that with one exception (that of the brown coal) there is an increase in gas production under the hydrogenation conditions. It should be stated, however, that in the “blank” experiments in

nitrogen the amount of gas evolved has been found frequently to be greater than that evolved under the conditions of the assay test. The methane is, as a rule, greater, also the carbon dioxide and the carbon monoxide is less. This increased gaseous production is, no doubt, due to cracking as a result of the relatively prolonged period of heating. The gas production after the hydrogenation tests has, however, in nearly all cases been found to be greater than in the blank experiment. The increase is most marked in the methane production, amounting to as much as 13 per cent by weight of the coal in one case (sample No. 12). In the assay tests the methane was found to be on the average about 50 per cent by volume of the gases given off at 450°C. except in the case of brown coal and lignite and several of the lignituous coals from which a considerable amount of carbon dioxide and carbon monoxide was obtained. In the gaseous products from hydrogenation, methane forms anywhere from 50 to 80 per cent of the mixture.

Table III gives the proximate and ultimate analyses of a number of the products A and B and, in some cases, C. From these it will be seen that a considerable amount of oxygen present in the original coal has been removed. This has been due in part to distillation and also in great measure to the action of hydrogen. The product A is thus left richer in carbon and in most cases poorer in hydrogen. It is interesting to note that in the case of the carbonaceous specimen (No. 27) the hydrogen was, however, rather greater than in the original coal. The C/H ratio which is, in general, over 20 is in this case only 19.

It will be seen from Table III that product A has retained the greater proportion of the sulphur present in the original coal but less of the nitrogen. The volatile matter is in most cases between 12 and 16 per cent and is, no doubt, influenced by the ash, practically the whole of which is left in the residue A. Assay tests have shown a certain uniformity in the quantities of coke produced and oil and water evolved at 600°C. The coke (in some cases coherent) amounted to approximately 90 per cent of the residue, the oil to 3 per cent and the water to between 3 and 6 per cent. The quantity of gas which has been found to be given off is of the order of 3 to 4 per cent by weight and the greater amount of this is free hydrogen. From these results one must conclude that the coke left at 600°C. will be practically devoid of oxygen and will contain only about 2.5 per cent of hydrogen. Product B is a brown powder contain-



5	Recent Lignite, Devon, coke at 430°C. Product A (solid). Product B (solid). Product C (liquid).	H <sub>2</sub> H <sub>2</sub> H <sub>2</sub>	1.01 0.97 0.88 —	4.01 12.12 1.02 —	41.8 15.6 36.13 —	80.42 90.59 86.79 88.63	4.56 4.38 4.66 6.36	0.28 0.27 0.58 0.30	1.11 1.31 0.09 0.06	13.63 3.45 7.88 4.65	17.6 20.7 18.6 13.9	Skinner and Graham ( <i>Fuel</i> , 1925, p. 474)
8	Vitrain, Slate Seam, Warwickshire. Product A (solid). Product B (solid).	H <sub>2</sub> H <sub>2</sub>	8.75 0.80 1.13	2.16 6.62 1.19	36.61 14.09 30.66	79.83 85.91 87.15	5.74 4.24 4.71	1.29 — —	1.11 — —	12.03 20.3 18.5	13.9	Skinner and Graham in course of pub- lication in <i>Fuel</i>
9	Ell Spires, Warwickshire. Product A (solid). Product B (solid).	H <sub>2</sub> H <sub>2</sub>	5.22 1.22 0.89	9.70 20.84 1.02	38.7 14.20 30.70	80.16 — —	5.76 — —	1.00 — —	1.36 — —	11.72 — —	13.9	Skinner and Graham in course of pub- lication in <i>Fuel</i>
10	South Staffs. Thick Coal, White Seam Clarain. Product A (solid). Product B (solid). Product C (liquid).	H <sub>2</sub> H <sub>2</sub> H <sub>2</sub>	13.26 4.00 2.94 nil	1.44 8.55 5.70 nil	33.37 — — —	81.25 89.23 90.09 85.98	5.27 3.76 4.90 7.59	1.25 0.99 1.26 1.12	0.94 3.57 0.27 0.01	11.29 2.45 3.48 5.30	15.4 23.4 18.4 11.3	Shatwell and Graham ( <i>Fuel</i> , 1925, p. 25)
11	Durain. Product A (solid). Product B (solid). Product C (liquid).	H <sub>2</sub> H <sub>2</sub> H <sub>2</sub>	6.06 3.15 2.98 —	3.50 4.80 1.19 —	31.18 — — —	82.44 89.74 92.20 86.20	5.08 3.97 4.95 7.73	1.04 0.74 1.20 1.20	0.72 2.51 0.78 0.01	10.72 3.04 0.87 4.86	16.2 22.6 18.6 11.1	Shatwell and Graham ( <i>Fuel</i> , 1925, p. 25)
12	No. 1 Seam, Somerset. Product A (solid). Product B (solid).	H <sub>2</sub> H <sub>2</sub>	1.74 0.29 1.86	3.65 14.77 3.89	34.36 16.25 33.91	81.71 87.74 88.10	5.32 3.88 4.67	1.49 1.39 —	1.54 3.34 —	9.94 3.65 —	15.4 22.6 18.9	Skinner and Graham in course of pub- lication in <i>Fuel</i>

TABLE III—Continued

NUMBER	COAL	TREATMENT	PROXIMATE PER CENT			ULTIMATE PER CENT (ASH-FREE DRY BASIS)					C/H RATIO	REFERENCE
			Moisture	Ash	Volatile	Carbon	Hydrogen	Nitrogen	Sulphur	Oxygen		
16	High Delf, Gloucestershire.....		4.33	4.43	35.27	83.77	5.56	1.10	1.36	8.21	15.1	Skinner and Graham in course of pub- lication in <i>Fuel</i>
	Product A (solid).....	H <sub>2</sub>	1.04	12.01	15.06							
	Product B (solid).....	H <sub>2</sub>	0.91	1.20	32.98	87.10	4.31				20.3	
17	Nottingham Top Hard, Soft Coal.....		11.53	4.89	31.22	81.55	4.76	1.76	1.61	10.32	17.1	Skinner and Graham in course of pub- lication in <i>Fuel</i>
	Product A (solid).....	H <sub>2</sub>	1.24	9.96	12.81							
	Product B (solid).....	H <sub>2</sub>	1.11	4.20	29.90	82.28	4.94				16.7	
20	Arley Seam, Lancs.....		1.92	2.87	33.68	84.19	5.47	1.86	1.79	6.69	15.4	Shatwell and Bowen ( <i>Fuel</i> , 1925, p. 252)
	Product A (solid).....	H <sub>2</sub>	0.62	16.54	15.92	85.86	3.93	1.54	6.51	2.16	21.8	
	Product B (solid).....	H <sub>2</sub>	—	—	—	87.60	4.56	1.73	0.35	5.76	19.2	
	Product C (liquid).....	H <sub>2</sub>	—	—	—	87.08	7.06	1.68	0.40	3.78	12.3	
	Product A.....	N <sub>2</sub>	0.65	5.02	15.45	89.09	3.59	1.14	1.10	5.08	24.8	
21	Wing Vein, South Wales.....		0.85	3.41	32.61	85.77	5.11	1.59	0.79	6.74	16.8	Skinner and Graham in course of pub- lication in <i>Fuel</i>
	Product A (solid).....	H <sub>2</sub>	0.31	18.28	15.17	89.89	3.88	1.50	2.54	2.19	23.2	
	Product B (solid).....	H <sub>2</sub>	2.12	2.54	33.64	89.01	4.54				19.6	

22	Cockshead, North Staffs. Product A (solid) Product B (solid)	H <sub>2</sub> H <sub>2</sub>	1.06 1.27 0.72	2.65 30.01 1.11	34.38 14.90 33.70	85.81 90.01 88.88	5.22 3.90 4.57	1.95 1.61	0.54 1.72	6.48 2.76 19.4	16.4 23.1 19.4	Skinner and Graham in course of pub- lication in <i>Fuel</i>
25	Nine Feet, South Wales. Product A (solid) Product B (solid)	H <sub>2</sub> H <sub>2</sub>	1.68 0.92 0.71	2.81 7.34 1.64	17.26 13.39 28.99	87.80 90.01 88.88	4.63 1.28	0.85		5.44 19.0		Skinner and Graham in course of pub- lication in <i>Fuel</i>
26	Deep Seam, Kent. Product A (solid) Product B (solid)	H <sub>2</sub> H <sub>2</sub>	1.71 1.11 1.02	6.85 15.34 1.37	20.63 11.47 33.24	89.66 90.01 88.88	4.60	1.36	1.84	2.54 19.5		Skinner and Graham in course of pub- lication in <i>Fuel</i>
27	Graigola. Product A (solid) Product B (solid) Product C (liquid)	H <sub>2</sub> H <sub>2</sub> H <sub>2</sub>	1.36 5.13 2.66 —	6.76 13.32 1.68 —	13.28 — — —	91.54 91.30 91.68 87.30	4.32 4.80 5.21 7.60	1.45 1.36 1.80 0.89	0.84 1.56 0.50 0.58	1.85 0.98 0.81 3.63	21.2 19.0 17.6 11.5	Shatwell and Graham ( <i>Fuel</i> , 1925, p. 25)
28	Hughes Vein, South Wales. Product A (solid) Product B (solid)	H <sub>2</sub> H <sub>2</sub>	3.07 0.97 0.66	3.61 7.88 3.37	11.64 9.32 23.87	91.43 90.01 88.93	3.87 1.10	1.00		2.60 23.6 19.1		Skinner and Graham in course of pub- lication in <i>Fuel</i>

ing 85 to 90 per cent carbon, 4.3 to 4.7 per cent hydrogen and between 0.8 and 6 per cent oxygen (except in the case of the lignite and brown coal when the product contained nearly 8 per cent). The amount of oxygen in this product no doubt depends to a certain extent on the oxygen content of the original coal. The nitrogen is rather higher and the sulphur considerably lower than is found in the original coal. The C/H ratio it will be seen (Table III) is usually about 19. The volatile matter is, with one or two exceptions, about 33 per cent.

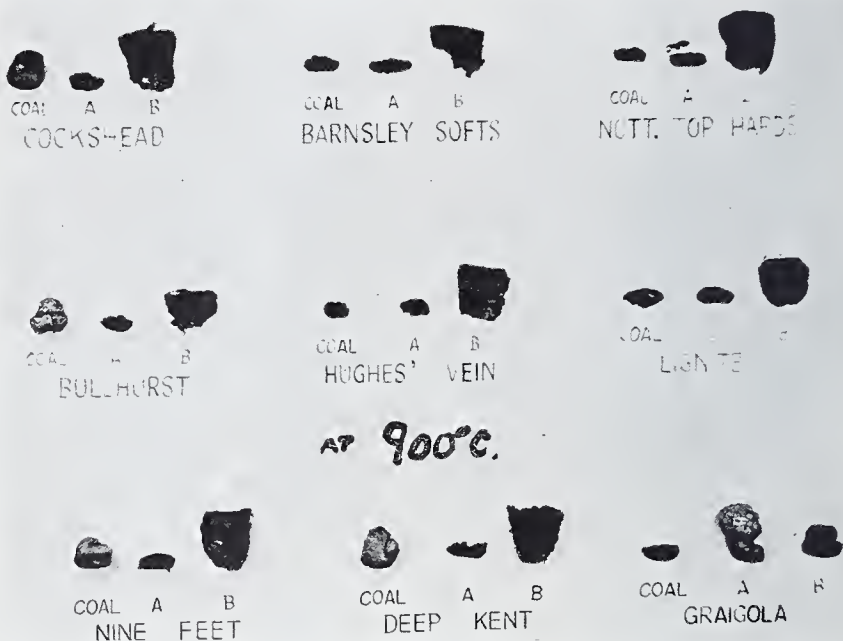


FIG. 6. SHOWING COKES OBTAINED FROM COALS AND SOLID HYDROGENATION PRODUCTS

On destructive distillation at 600°C. about 85 per cent was, in general, left as coke, and 7 to 8 per cent of oil and about 2 per cent of water evolved. The product from the Graigola coal (No. 27) differed somewhat in giving about double the quantity of oil (15 per cent) and in having a lower C/H ratio (17.6). The amount of gas evolved from this product from the various coals has not been so great as from A but here again hydrogen forms the main constituent. When heated in a tube softening has been observed in most cases at a temperature between 270° and 310°C. and decom-

position set in between  $330^{\circ}$  to  $340^{\circ}\text{C}$ . with evolution of oil or phenol. When dissolved in phenol and heated in an autoclave in presence of nitrogen decomposition also took place to a small extent and a material insoluble in phenol was formed. The fact that decomposition occurred at a temperature below that employed in the hydrogenation experiments points to the fact that this intermediate compound is only stable at temperatures above  $250^{\circ}\text{C}$ . and up to  $430^{\circ}\text{C}$ . in presence of a high concentration of hydrogen molecules.

The cokes formed at  $450^{\circ}$ ,  $600^{\circ}$  and  $900^{\circ}\text{C}$ . are all strongly swollen but fragile. Figures 6 and 7 illustrate the form of coke produced at

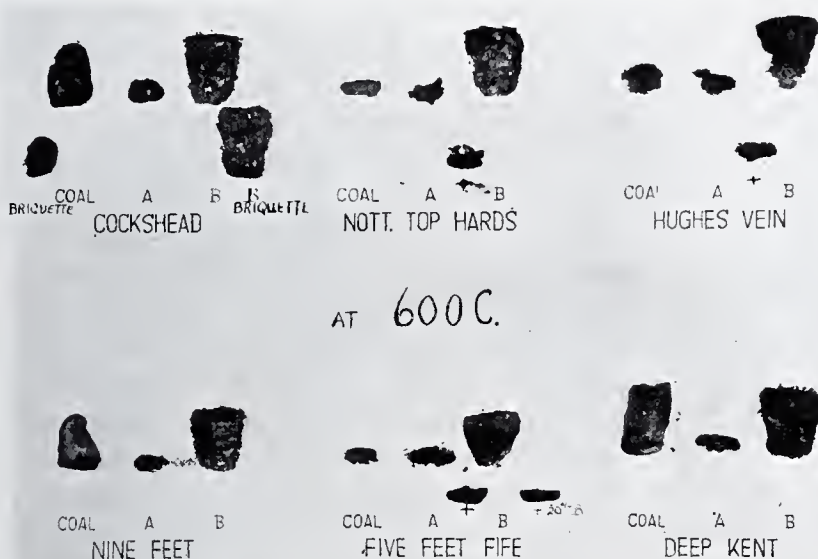


FIG. 7. SHOWING COKES OBTAINED FROM COALS AND SOLID HYDROGENATION PRODUCTS

$600^{\circ}$  and  $900^{\circ}\text{C}$ . (by heating 0.5 to 1 gram in a platinum crucible as in the ordinary volatile matter test) from products A and B and in some cases mixtures of these in the proportion in which they were found during hydrogenation. The coke residue from the ordinary coal is also shown for comparison in each case. In most cases the "coke" formed from the residue (A) was only a powder but in one or two cases was coherent and somewhat stronger even than that from the original coal. This was so in the case of coal No. 24, coked at  $600^{\circ}\text{C}$ . In all cases product B gave a very swollen coke. When A and B were mixed in the proportion formed by hydrogenation, a

coke stronger than that from A was formed and usually much stronger than that from the original coal. This was especially so in the case where the coal used was of the non-coking variety (Nos. 18, 24 and 28). It was thought that possibly the very fine state of division of the powder might be responsible, to a certain extent, for the swollen character of the coke. A compressed briquette of the material gave, however, a similar coke, and the very swollen coke is, therefore, characteristic of the product itself.

Apart from No. 27, it is evident that considerable uniformity in analytical characteristics and behavior exists among the residues (A) obtained from the different coals and that a similar uniformity is shown by the portion (B), soluble in phenol and insoluble in chloroform. Product B has been found to be almost completely soluble in pyridine.

The investigation of these products is of great interest and will, I feel convinced, be exceedingly helpful in the elucidation of the constitution of coal and of those constituents responsible for coking. Product B, as a substance obviously more simple in constitution than the original coal, should be of particular help in this respect.

It will be noted that the residue (A) from the Graigola coal (No. 27) gave a coke similar to those from the B products in other cases and even more swollen than the B product from the Graigola coal itself. It has already been pointed out how the products from this coal have differed from the majority of the corresponding products from other coals. In this case (No. 27) hydrogenation products have been formed which are insoluble in phenol and yet contain a higher percentage of hydrogen than the residue obtained in the case of other coals. The effect of this upon the coking quality is very evident. Hydrogenation has in this case produced a coking material insoluble in phenol. Again by referring to the analysis of product B from this coal it can be seen that a larger percentage of hydrogen is present in this than in other of the B products. In this case the hydrogenation would appear to have gone further but not sufficiently far to produce those compounds (no doubt less complex and of lower molecular weight) which are soluble in chloroform.

It has been mentioned that in some of the early experiments a strong coke was formed after partial hydrogenation of clarain from the South Staffordshire Thick Coal, the quantity of hydrogen absorbed being only about 1.5 per cent (by weight) of the coal.

During the past year members of the staff of the Fuel Research

Board have investigated at Greenwich<sup>3</sup> the question of the partial hydrogenation of coal and have produced a good coke from a non-caking coal and from anthracite. The explanation of this lies, I believe, in the formation of those compounds which we have been considering, namely the product B and also hydrogenation products similar to those found in the residue from coal No. 27. How far these products may be converted into oil, future experiments will, I hope, show.

Product C has been fractionally distilled in every case and is by no means composed of hydrocarbons only. Where analyses have been given in Table III it will be seen that about four per cent of oxygen is usually present in the crude product. Undoubtedly further hydrogenation in the presence of a suitable catalyst will yield a high percentage of pure hydrocarbons. It has been pointed out that the nature of our treatment has given no indication of the quantity of phenols produced during the process. Tests carried out by Bowen and Nash<sup>4</sup> on the catalytic hydrogenation of Arley Coal (No. 20) have shown that the amount of phenol produced under these conditions formed 3 to 4 per cent of the coal. Fischer and Frey found in the case of brown coal that about 10 per cent of the coal was converted into phenols. The production of phenols during the hydrogenation of the many other samples tested by us may, I believe, be taken as under 3 per cent of the coal.

It was mentioned at the commencement of this paper that examination of the macroscopic constituents of coal formed part of our program of hydrogenation. The results from two of the macroscopic constituents of a South Staffordshire coal have been included in Tables I and II and from these it will be seen that the Clarain gave the greatest oil yield. No. 9 (Ell Spires) is mainly composed of durain and comes from the seam contiguous to that from which No. 8 (vitrain) was taken. It will be seen that there is little difference between the amounts of the two residues. Fusain was found to be incapable of reacting to any appreciable extent with hydrogen under the conditions of our tests. Examination of the products obtained by the separation of coal with solvents will, I believe, prove to be of greater interest. Two cases have been tested so far in this way. One (No. 19) by extraction with pyridine, the other (No. 8) by phenol. The quantity extracted in the two cases was 25.6 and

<sup>3</sup> Report of Fuel Research Board for period ended March 31, 1928.

<sup>4</sup> Fuel, 1926, pp. 361-364.

14.0 per cent respectively. Only the residue left after extraction has in each case been tested up to the present. The residue after extraction of the vitrain with phenol left material amounting to 36 per cent of the ash-free dry coal against 48.8 per cent left after hydrogenation of the coal. It would thus appear that during the hydrogenation of the extract, most of the latter must be unattacked and be left as a residue in order to make up the amount formed. On the other hand, the residue from the pyridine extraction yielded an amount of residue after hydrogenation (calculated to ash-free dry coal) practically equal to that of the residue obtained by direct hydrogenation of the coal (22.5 and 24.5 per cent respectively). It seems legitimate to conclude, therefore, that the greater proportion of the pyridine extract is converted into oil, as well as a considerable proportion of the  $\alpha$  portion of the coal. This part of our investigations is, however, only at its initial stage and further discussion is reserved until more experimental evidence is available.

The original claims of Bergius insisted that the absorption of hydrogen was not the result of the use of a specific catalytic agent. It is well known, however, that Bergius uses an iron compound which is incorporated in his coal-oil paste (Luxmasse) ostensibly for the purpose of removal of sulphur. From the results of our experiments we are convinced that considerable liquefaction of the coal occurs without the use of added catalysts. In view of the use of oxides of iron by Bergius and of the many patents taken out by the I. G. in regard to the use of diverse reagents as catalysts in the hydrogenation process, we have thought it worth while to study the influence of a number of metallic derivatives, when mixed with the coal. The use of 5 per cent  $\text{Fe}_2\text{O}_3$  produced an increase of 2 or 3 per cent in oil yield in the case of some coals, more especially those which did not produce a high yield without the catalyst. In the case of No. 22, practically no change in amount of the products was found. Bowen and Nash<sup>5</sup> had previously tested the comparative effect of nickel oxide and iron oxide in the hydrogenation of Arley coal in the absence of a suspending medium. Their results showed the marked superiority of nickel oxide as a catalyst although the yield of oil was not so great as when the coal was treated with phenol but without a catalyst. In our experiments, phenol has been used as suspending liquid even in the presence of a catalyst.

With coal No. 22, nickel oxide gave an increase of 4 per cent in light

<sup>5</sup> Fuel, 1926, pp. 361-364.

spirit, of over 14 per cent in the tar-oil and almost halved the amount of product B, while reducing the residue from 18 to 7.2 per cent. The amount of water was also increased considerably and although it is possible that part of the increased yield was produced by action of hydrogen on the phenol under the influence of the catalyst, nevertheless, the reduction in residue and product B indicated additional conversion of the coal.

With ammonium molybdate, D. G. Skinner has recently obtained a still greater conversion of the coal—only 5.5 per cent of residue (on ash-free dry basis) being left, and a yield of 12.6 per cent of light spirit and nearly 60 per cent of tar-oil being obtained.

Hlavica<sup>6</sup> has recently published results showing that the oxides of zinc, nickel, cobalt and copper are more effective than iron oxide, 30 to 100 per cent more oil being formed by the use of the former, whilst the reaction time was shortened to one-third and the quality of the oil improved. Neither the optimum temperature nor optimum pressure were, however, altered. The conclusion of this investigator is that the catalyst affects primarily the decomposition of the coal and only secondarily the actual hydrogenation.

We have also studied the influence of finely grinding the coal in a colloidal mill prior to hydrogenation and have found the yield of oil from a non-coking coal (No. 13) to be increased by about 4 per cent—a slightly increased amount of product B being also given. In the case of the coking coal (No. 22), however, the fine division of the particles apparently induced coking at the temperature of hydrogenation, and thus prevented the action of the hydrogen.

In referring again to Table I it will be seen that the yield of oil from Boghead cannel has not been increased materially under hydrogenation conditions over that obtained by ordinary distillation. Those constituents of molecular structure suitable for the addition of hydrogen would therefore appear to be absent from the boghead coal or torbanite (and from analogy one may conclude from the oil shales). On the other hand, the yield of oil from black cannel (occurring in bituminous coal seams and considered by Thiessen to consist largely of spores) was considerably greater than that obtained by distillation.

Concerning the application of our results to coals of the United States, it would appear that those of the "Eastern type of bituminous" in Parr's classification should be most readily acted upon

<sup>6</sup> Brennstoff-Chemie, 1928, 9, pp. 229-231.

by hydrogen under pressure. It has been shown that the meta-lignituous coals examined by us have, in the main, not given nearly such a high conversion. These coals correspond to the "Western type of bituminous" of Parr's classification. Although we can say that coals belonging to the parabituminous class will be readily acted upon by hydrogen, my belief is, however, that classification either by the Seyler method or that of Parr gives only a general idea

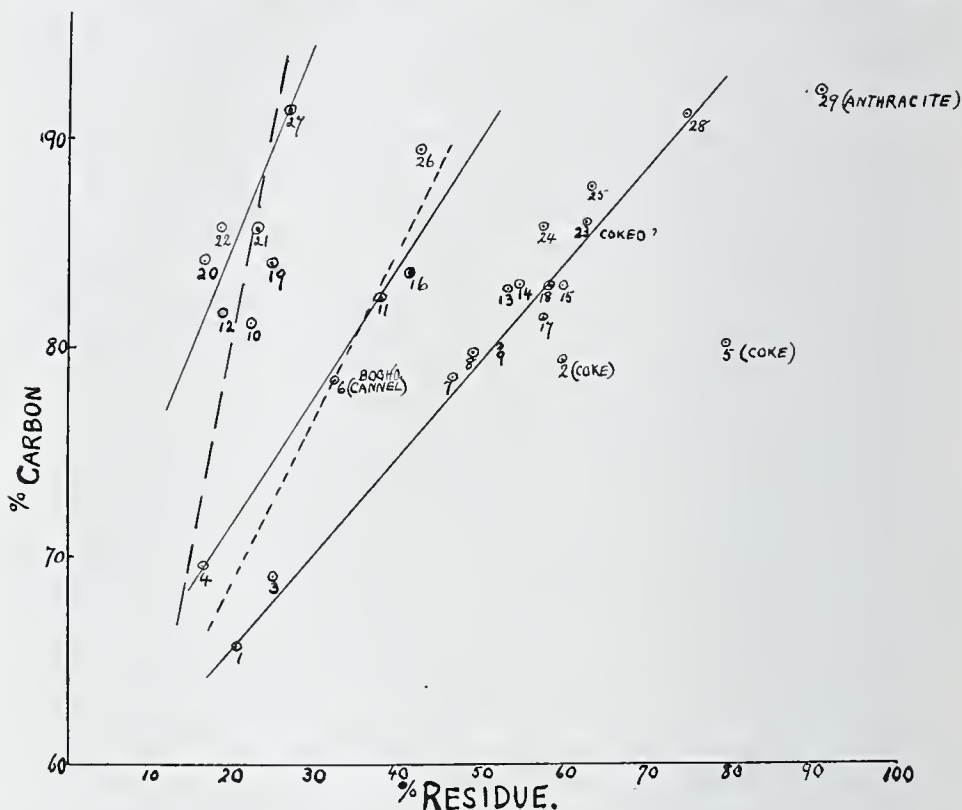


FIG. 8. ILLUSTRATING CONNECTION BETWEEN CARBON CONTENT AND EASE OF HYDROGENATION

regarding ease of hydrogenation, and that ultimate analysis alone is unable to forecast whether a coal may or may not be readily hydrogenated.

In order to find any further possible relation between the ease of hydrogenation and chemical composition I have plotted the amount of residue (which may be taken as a measure of reactivity with hydrogen) against such factors as C/H ratio,  $\frac{C}{H - \frac{O}{8}}$  ratio, moisture,

oxygen, and carbon content. The per cent carbon-residue graph has proved to be the most instructive and is therefore reproduced (Fig. 8). It will be seen that the coals fall into distinct groups lying upon diagonal lines which connect those of low with those of high carbon content.

During the "coalification" process loss of easily removable hydrogen and oxygen and a relatively smaller loss of carbon in the form of water, carbon dioxide and possibly methane, might be expected to take place without materially affecting the general chemical structure of the organic compounds of which the coal conglomerate is composed. Figure 8 may, I think, be interpreted as indicating that in certain of the geologically younger coals we may have particular types of compounds capable of ready hydrogenation and that the chemical structure of these may persist, thus rendering hydrogenation possible in some of the older, or higher rank, coals in spite of loss of oxygen and hydrogen and possibly carbon as a result of metamorphic change, whereas in the case of the coals not readily attacked by hydrogen the chemical structure of their non-reactive constituent compounds may likewise persist in those older coals which may possibly have been derived from them.

Following this line of reasoning it seems to me quite probable that coals 28 and 25 may have been formed, in the main, by further degradation of material composing coals 13, 14, 15, 7 or 8, and that these latter may have been derived from Nos. 1 and 3. A similar connection is, I think, shown between the two metalignituous coals 10 and 12, the parabituminous coals 19, 20, 21 and 22 and the ortho-carbonaceous specimen 27. The middle line passes through one or two coals of the metalignituous group and also through what we have termed "recent lignite." Although no doubt much altered in composition, as a result of metamorphic change, from the vegetable matter from which it had originated, this material still showed a marked woody structure. It was found to be easily disintegrated to a brown powder. Although Boghead Cannel also lies on this line, it is recognized that this material is quite distinct from the ordinarily coals, and I do not mean to imply its derivation from lignite. Its position in the graph is due to the fact that it yields a relatively small amount of residue when destructively distilled in the ordinary way. Thiessen's work has shown that this material has been formed in large part from algae. It is of course quite probable that the "dash" line through 4 and the group directly above may

express the trend of the degradation better than the full line drawn to connect this with coals Nos. 11, 16, and 26 and that the dotted line through 11, 16 and 26 may also be more representative of the bulk, indicating composition and characteristics mean between those coals lying in the neighborhood of the other two lines. Obviously in the present state of our knowledge, the direction and position of these connecting lines is very uncertain and I have simply drawn them to illustrate what, to my mind, is indicated by these results, namely that the connection between the ease of hydrogenation and certain coals and carbon content (or, in other words, geologic age of the coal), is due largely to the persistence through metamorphic change of readily hydrogenated molecular structures.

In view of the theory put forward by Wheeler and coworkers in regard to the ulmic character of the "reactive" constituents of coal—it is naturally of interest to see how far such a theory fits in with the results of our hydrogenation experiments. The amount of ulmin compounds in each coal has not yet been estimated (although it is intended to do this). In accordance with their theory, the ready oxidizability of certain coals is due to the presence of a large amount of ulmic bodies. Those coals lying on the right of the graph (Fig. 8) belong to this class, whilst such coals as Nos. 19, 20, 21 and 22 belong to a class whose members do not undergo oxidation readily at a temperature below 100°C. Dr. Wheeler was good enough to have some tests made for me three years ago in regard to ease of oxidation (with hydrogen peroxide), of some of the coals and their residues after hydrogenation. The results of these tests, which were carried out to ascertain whether the "reactive" (ulmin) substances were more readily attacked than the plant debris, were not very conclusive. In the case of some of the coals tested (Nos. 10 and 11), the plant debris appears to have been attacked as well as the ulmin portion, whilst in the case of No. 20 most of the plant debris was found in the residue after hydrogenation. It seems clear, however, that the most readily oxidizable coal ulmins are not the bodies which will give upon hydrogenation an oil or substance soluble in phenol; nor have the cokes which we have obtained from some of them (i.e., from the lignites) at low temperatures been shown to be so. Our results have shown that reactivity to hydrogen depends upon the source from which the coke has been derived and this has also been found by Fischer.

Ease of hydrogenation, I believe, depends upon the chemical consti-

tution of the complexes which make up the coal and such constitution must necessarily depend upon that of the original coal-forming matter and also upon the nature of the changes which have taken place during the coalification process. In hydrogenation, I believe, we have a means of obtaining considerably greater knowledge regarding the constitution of coal than has been possible with the means hitherto available, namely, by analysis, distillation and oxidation.

It has been shown by the investigations of various workers, including ourselves, that in general the greatest absorption of hydrogen occurs at the time of pyrogenic decomposition of certain constituents of the coal, i.e., the hydrogen becomes attached to the nascent unsaturated bonds thus formed, with the production of compounds which may be either solid, liquid or gaseous. To a certain extent direct hydrogenation is possible by prolonged action and probably such action is greatly facilitated by the addition of catalysts. With highly oxygenated coals the first action appears to be the removal of the greater part of the oxygen, leaving a residue which is frequently more strongly caking than the original coal. In some coals the easily hydrogenated constituents would appear to give oil as a direct result of the action of hydrogen, in other cases a solid product, such as the product B, in our tests, soluble in phenol or, as in the case of No. 27, a product insoluble in phenol and having different characteristics from those of the original coal. It is clear that the nature and quantity of the products of hydrogenation depend largely upon the chemical composition of the coal under test. Treatment by hydrogen under standard conditions of pressure and temperature should always yield valuable information and should, therefore, in my opinion, be included in any scheme for the rational analysis of coal.

In this paper I have by no means given a complete account of the subject of the hydrogenation of coal, nor have I referred to the excellent work in different countries of many of the investigators of this subject. I have simply attempted to put before this Conference those aspects of the subject upon which, as a result of our own experiments, I feel more capable of commenting, rather than the economic side of the question. In the latter the nature of the products is, of course, of vital importance. Once, however, it is possible to convert the major portion of the coal into crude oil or tar, the subsequent treatment of the latter for the production of more valuable products would now appear to be a matter of selection of a suitable catalyst. The production of gas in the quantity found in

this method of treatment need not be a great drawback in view of the now practical possibility of conversion of this by subsequent treatment into liquid products (benzene, etc.). The extension of our knowledge of the action of hydrogen under high pressure upon coal, either with or without a catalyst, has, in my opinion, given justification for the optimistic view held by the supporters of this method of treatment in regard to the eventual commercial success of the process. The surest way to the realization of this, lies, I believe, in the continuation of researches in which coal is not simply considered as a black mass containing so much carbon, hydrogen, oxygen etc. but rather as a mixture of molecular complexes each of which will behave in a definite way when subjected to hydrogenation, distillation or oxidation. Nevertheless we are all, and the technical world in particular, indebted to Dr. Friedrich Bergius for his part in the development of high pressure technique and for his pioneer work in the conversion of coal into oil by hydrogenation.

Before concluding I wish to record my indebtedness to Dr. J. S. Haldane, C.H., F.R.S., for his helpful criticism and to those members of the staff of the Mining Research Laboratory, whose work has made it possible for me to place these results before this Conference, in particular Mr. D. G. Skinner. I am glad to have this opportunity of expressing my thanks to the President and Advisory Board of the Carnegie Institute of Technology for their invitation to take part in this important Conference.

# A NEW METHOD FOR THE DIRECT DETERMINATION OF THE REST TEMPERATURE OF HYDROGENA- TION FOR BITUMINOUS COALS

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## INTRODUCTION

Up to this day the temperature of hydrogenation has had to be established by long and arduous groping. This temperature is a preponderant factor which influences especially the yields in oils and varies from one coal to another. When the temperatures used for the different corresponding yields were placed side by side, the one which seemed to guarantee the best economic yield was arbitrarily chosen. But indecision prevailed on account of the unknown that could be eliminated only by a direct or indirect relation.

Taking account of the chemical character of coals we have tried to discover and to determine thermal points which exist and vary from one coal to another. For different reasons, to which we shall return in a subsequent study, we have given up this method in favor of expansion which is more simple to determine and more obvious to interpret.

The first deviation of the expansion curve indicates the first appreciable attack of hydrogenation (Fig. 1). The molecular decomposition progresses, and at the temperature when the rate of expansion reaches its maximum, hydrogenation gives the greatest yields in oils and always the maximum of light gasoline.

*A. The Measurement of the Expansion of Coal under the Action of Destructive Distillation.* This measurement requires that the substance be in powdered form in order to avoid the difficulties of a measurement of the cubical expansion of a substance that is splitting up. A quartz tube, 15 mm. in diameter is filled and closed at its bottom with successive equally thick layers, in order to obtain a total height of 25 mm. A quartz tube serving to register the expansion rests on the coal through the intermediary of a refractory disk. A multiplying lever serves to amplify the ascending movement of the rod.

The quartz tube containing the coal was heated rather slowly in an electric furnace in order that the heating in the interior of the mass

of coal should be approximately uniform. The total duration of a run was two hours.

The observations made in the course of tests, shown in Figure 1, have served to determine (a) the curve of the total expansion, and (b) the curve of the expansion velocities during the different phases of the run. They are shown in the appended table.

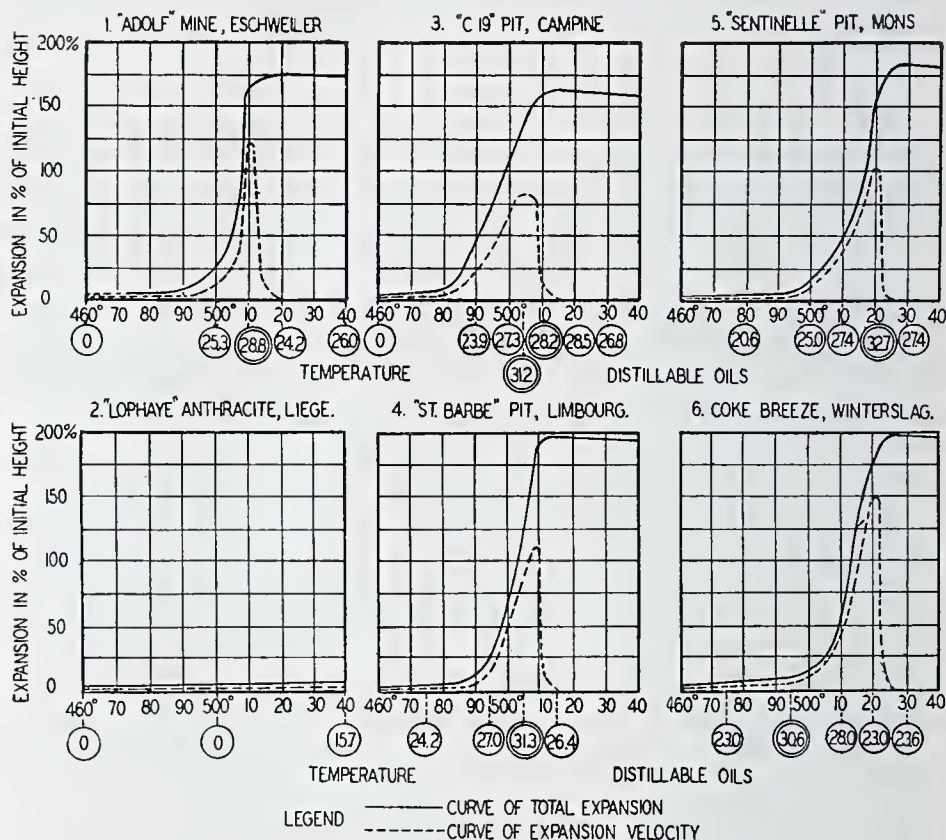


FIG. 1

*B. The Curves of the Total Expansion.* These curves show the total increase in height caused by the swelling of the coal. This swelling may reach two hundred per cent of the initial height.

It is noticed that the magnitude of the expansion does not depend directly on the content in volatile substances freed during the heating tests, but rather on the nature and origin of the coal. (See the chemical relations in Table I.)

Coal 4 and 6 differing by 8 per cent in volatile matter content show practically the same expansion.

The anthracite coal (No. 2) scarcely undergoes any expansion. This method of testing gives us then a very efficacious and scientific means of differentiating coals that burn with a bright flame and anthracitic coals.

For coals burning with a bright flame all the expansion curves show a rapidly rising slope proving that the swelling and consequently the interior expansion, occur in a very short interval of time (Fig. 1).

This interval, which is so clearly marked, is a remarkable characteristic for each kind of coal.

*C. The Expansion Velocity Curves.* These curves traced in a dotted line below the expansion curves show the linear velocity with which the swelling occurs at each moment of the test. In general, the letter begins gently without a definitely marked starting point; it rises, then, with an increasing speed up to a maximum and from here the expansion diminishes rapidly. It stops in less than two minutes after the maximum liberation.

This very pronounced maximum indicates the most intense moment of the molecular decomposition, and at the corresponding temperature the hydrogenation yields the maximum of oils and always the maximum of light gasolines, unless it is a question of mixtures. We have here the confirmation of the fact that the maximum molecular decomposition must correspond to the maximum expansion velocity.

Let us note that the velocity curves show more marked differences than the expansion curves. The greater the content in volatile substances is, the longer is the interval during which the distillation occurs, but also the better are the general contributions of the hydrogenation. The decomposition of coals rich in volatile substances is accordingly less turbulent and more regular than that of coals less rich in gases (Nos. 1 and 6) whose decomposition is more abrupt but of shorter duration. And in this way the curve of the expansion velocity is a scientific means to reveal the sensibility of such and such a coal for hydrogenation.

*D. The Relations of Hydrogenation to the Measurements of Expansion.* The influence of the hydrogenation temperature is shown by tests recorded in Figure 1 and Table I. But what we must remember and what we wish to show is that the results are in perfect relation with the maximum of expansion velocity.

It is shown, in general, that the maximum yield of all oils is, moreover, characterized by the highest content in light gasolines. After the temperature of the maximum speed of decomposition has been

TABLE I

PYROGENOUS EXPANSION OF COALS AND VARIATIONS IN YIELD, OBTAINED BY BERGINIZATION AT DIFFERENT TEMPERATURES CORRESPONDING TO THE CURVE OF EXPANSION

CHARACTERISTICS, CHEMICAL COMPOSITION OF THE COAL											EXPANSION TEST		BERGINIZATION TEST					REMARKS		
NUMBER	NAME AND ORIGIN OF COAL	Water	Volatile substance	Ash	C	H	N	O	S	Heat value	Progress of expansion	Corresponding temperatures	Oils obtained per 100 grams of paste							
													Temperature	Fraction 0-230°	Fraction 230-330°	Total oils	Coal tar		Insoluble organic matter	
1	Adolf Mine (Eschweiler)	3.0%	23.8%	4.7%	83.3	5.43	1.56	4.17	0.83	7736 (7449)	Beginning	485°	450°					Thick Berginizzate		
											Maxima speed	510°	500	12.1%	13.2%	25.3%	35.4%	16.9%	Non-distillable viscous Berginizzate	
											End	520°	510°	16.9	11.9	28.8	36.0	18.3	Liquid Berginizzate	
													520°	15.0	9.2	24.2	21.7	37.7	Part coke Berginizzate	
													550°	17.0	9.0	26.0	20.0	24.3	Part coke Berginizzate	
2	Lophaye Anthracite (Liege)		7.5	2.0	87.5	5.34	1.34	3.02	0.74	8289 (8003)	Beginning	No clearly marked figure	450°	Non-distillable					Non-distillable Berginizzate	
											Maxima speed		500°	Non-distillable					Non-distillable Berginizzate	
											End		550°	8.7	7.0	15.7	11.1	70.6	Pasty Berginizzate	
		0.71	31.1	6.4	78.75	5.63	1.18	5.12	0.92	7719 (7417)	Beginning	480°	460°	Non-distillable					Non-distillable Berginizzate	
											Maxima speed	505°	490°	13.7	10.2	23.9	29.3	21.0	Viscous Berginizzate	
3	Charbonnage des Liégeois "C.19" (Campine)										End	515°	500°	17.9	9.4	27.3	27.6	24.4	Liquid Berginizzate	
														505°	20.0	11.2	31.2	25.1	33.7	Liquid Berginizzate
														510°	16.3	11.9	28.2	31.2	15.3	Liquid Berginizzate
														520°	18.36	10.2	28.56	26.0	26.3	Berginizzate with coking residue
														530°	16.97	9.8	26.77	24.0	37.4	Berginizzate with coking residue
4	Limbourg Pits S. Barbe Eyden (Meuse)		23.6	6.4	77.03	5.17	1.37	9.04	0.99	7500 (7223)	Beginning	490°	475°	12.8	11.4	24.2	46.7	17.2	Viscous Berginizzate	
											Maxima speed	510°	495°	17.8	9.2	27.0	31.2	23.3	Liquid Berginizzate	
											End	515°	505°	21.4	9.9	31.3	27.9	23.4	Liquid Berginizzate	
													515°	15.9	10.5	26.4	22.3	34.8	Liquid Berginizzate	

5	"Sentinelle Pigs" (Mons)	27.1	2.08	83.72	5.80	1.48	6.48	0.44	7904 (7593)	Beginning Maxima speed End	490° 520° 525°	480° 500° 510° 520° 530°	9.3 15.8 16.8 21.5 17.2	11.3 9.2 10.6 11.2 10.2	20.6 25.0 27.4 32.7 27.4	54.7 27.4 23.3 23.5 26.0	17.1 35.1 33.7 29.2 31.1	Pasty Berginizate Liquid, coking residue Berginizate Liquid Berginizate Liquid Berginizate Liquid Berginizate residue of coking	with
6	Coke Breeze Winterslag.	19.8	10.2	76.28	6.30	1.34	5.03	0.85	7113 (6775)	Beginning Maxima speed End	495° 520° 525°	475° 495° 510° 520° 530°	11.9 19.2 18.8 14.2 16.7	11.1 11.4 9.14 8.8 6.9	23.0 30.6 28.0 23.0 23.6	46.1 28.3 24.5 27.7 21.7	12.8 15.7 28.3 33.9 38.5	Viscous Berginizate Liquid Berginizate Liquid Berginizate Liquid Berginizate coking residue Liquid Berginizate coking residue	with

passed, the light gasolines diminish quickly, more quickly than the additional increase which would be expected from the corresponding cracking of the medium oils and of the coal tar (Fig. 1 and Table I). Without entering into details we may keep in mind that we have now the possibility of seeing the gliding reactions of the cracking and syntheses in relation to a fixed point.

The Winterslag coal forms an exception. The maximum yield of all oils is not obtained at the temperature of the maximum speed of decomposition which is at  $520^{\circ}\text{C}$ . but at  $495^{\circ}$ . But this coal is a mixture, and trial tests must yet specify the influence of mixtures, or if there are some coals in which the hydrogen interferes in a secondary state. In five cases out of six of tested coals, hydrogen does not influence the direct relation between the maximum of expansion velocity and the maximum yield of oil. Do the mixtures of coal follow the laws of alloys in that the molecular decomposition is lowered by the number of the constituents like the liquefying point of an alloy. This question is being studied in our research laboratory and will soon be settled.

But we still recognize the base prepared by a more suitable method for a more scientific classification of coal. And we introduce a fixed point between two kinds of reactions, whose differentiation has been impossible until now. I mean the differentiation of the cracking and the synthesis.

#### CONCLUSION

The study of the destructive distillation of coals shows valuable relations for hydrogenation whose results are in correlation with the maximum speed of expansion, i.e., with the maximum speed of molecular decomposition.

These relations show:

1. The temperature interval in which the coal can be hydrogenized.
2. The temperature to be used to obtain a maximum yield in benzines.
3. The degree of suitability of a coal for hydrogenation and its suitability to form mixtures with a view of lowering the hydrogenation temperature increasing the interval.

## THE HYDROGENATION OF PITCH AND ASPHALT

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The classical experiments of Sabatier and his collaborators on catalytic hydrogenation in the presence of finely divided metals have been extended to a great number of organic substances. First the simplest substances were studied, and then this method was applied successfully to more and more complex substances of high molecular weights, of a colloidal nature and of unknown constitution.

On the one hand, there were perfected methods of hydrogenation in a gaseous system according to Sabatier, and in a liquid system according to Ipatiev and Broche; on the other hand, the catalyzers used were perfected in each particular case.

The hydrogenation of pitch is one of these cases. It can be considered from the special angle of the hydrogenation of solid combustibles. This is a timely question the answer to which consists in the transformation of solid combustibles into liquid combustibles.

In fact, the ratio of hydrogen to the total carbon and oxygen is clearly lower in solid combustibles than in liquid combustibles. One may, then, hope to pass by hydrogenation from the first to the second.

The fixation of hydrogen in the pitch by means of customary processes is not possible, because the known catalyzers, consisting of reduced metals such as platinum, nickel, copper, or iron are rapidly poisoned by the presence of sulphur. The extremely complicated colloidal composition of pitch increases the difficulties still more.

The Bergius process of hydrogenation under high pressures without catalyzers is applicable to pitch. Moreover, this application is the subject of his patents.

Here are the results that we have obtained with a coke oven tar:

This pitch yields in destructive distillation under the ordinary pressure 43.8 per cent of liquid products in the range of from 50 to 350 degrees.

After hydrogenating for ten hours at 480° under a hydrogen pressure which at ordinary temperature measured 100 kgm., 5.17 per cent of the hydrogen was absorbed and the product transformed into a liquid tar.

This tar yielded at distillation:

	Per cent	Residue per cent	
50-250°	16.5	tar	15.0
250-300°	12.0	coke	27.0
300-350°	16.0	losses	0.5
350-400°	13.0		
<hr/>			
57.5 (distilled)			

The results are very good. There is, however, an amount equal to 43 per cent which escapes hydrogenation, and cannot be transformed even under the best conditions.

There are in the pitch some very heavy products that are characterized by a rather high content in oxygen, are very sensitive to heat and which coke easily. That it is difficult to hydrogenate these bodies is seen clearly from a German patent by Mr. Klever, one of the collaborators of Bergius. He attempted to separate these products by using a very high vacuum. The oily bitumen which distills under these conditions without decomposition is then subjected to a catalytic hydrogenation. Almost all the substances of mineral chemistry are claimed to be hydrogenation catalyzers, especially platinum and nickel. We have already given our opinion of these catalyzers.

The English patent 213161 for the hydrogenation of pitch in the presence of alkaline metals such as sodium or calcium, doubtless indicates progress. Sodium is added for the purpose of desulphurization. But at the same time a favorable action in the process of hydrogenation is seen. We have convinced ourselves, however, that the yield in liquid products is not higher on account of the addition of sodium, than that which we have mentioned before.

Quite recently there was published an English patent (EP. 277-974 of December 21, 1927) of A. Spilker and C. Zerbe and *Gesellschaft für Teerverwertung*, in which hydriodic acid is recommended as a catalyzer. It is claimed that pitch would yield under these conditions, 20 per cent of hydrocarbons boiling up to 200°, 30 per cent Diesel engine oil, and 20 per cent of lubricating greases. The yield would rise to 70 per cent.

We used the hydrides of alkaline and alkaline earth metals, such as those of sodium, potassium, and calcium, as catalyzers.

The alkaline and alkaline earth metals combine with hydrogen at temperatures above 200° to give saline hydrides of the formula MeH or MeH<sub>2</sub>. These are white crystalline powders dissociable at high

temperatures in a vacuum. The hydrides are, in general, very active and sensitive to the oxygen and humidity of the air, but they can be handled without danger if proper precautions are taken.

Considering the special constitution of these hydrides in which hydrogen appears as an anion, and the fact that these hydrides begin to dissociate a little above the temperature of their formation, one may attribute to them a certain mobility of hydrogen, which would permit their use as agents of hydrogenation.

Several indications of this opinion are found in literature:

Maier and Altmaier (B. 41, 1908, p. 3079) hydrogenized carbon to form methane at a temperature above  $270^{\circ}$  in a mixture containing the hydride of calcium. A residue of calcium carbide remained.

Durand and Shervill Haughton (*C. v. l'Acad. des Sciences*, 180, p. 1934) reduced nitrated derivatives with hydride of calcium. The calcium was recovered in the form of the oxide.

Reich and Serpek (*Helvetica Chimica Acta*, 3, 1920, p. 138) passed carbon monoxide or carbon dioxide gas over calcium hydride, and obtained methane, calcium carbide, and calcium oxide.

Contrary to the supposition that we made, it seems to us that the hydrogen of the alkaline and alkaline earth hydrides is rather firmly fixed and is not very suitable for hydrogenation.

Thus it is quite unexpected to see that these hydrides transmit hydrogen under hydrogen pressure as easily as the nickel does in Sabatier's catalytic hydrogenation.

Naphthalene can be hydrogenated in the presence of sodium hydride under the same conditions as with nickel, under a hydrogen pressure of from 10 to 20 kgm. and a temperature of  $230$  to  $250^{\circ}$ . In hydrogenating pure naphthalene, it is found that the hydride of sodium remains unchanged. The sole product of the reaction is tetrahydronaphthalene.

For this reaction one proceeds in the following manner:

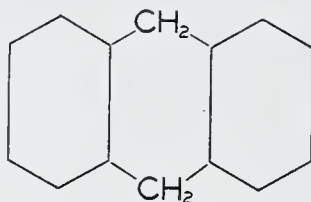
Sodium (equal to two to three per cent of the quantity of naphthalene) is introduced into an autoclave equipped with an agitator, and heated under hydrogen pressure. The absorption begins a little above  $200^{\circ}$ . It is rapid, and complete at  $260^{\circ}$  to  $270^{\circ}$ . If the pressure is not too strong (20 kgm.), it corresponds to an atom of hydrogen for an atom of sodium. Under very strong pressures (100 kgm.) the absorption is greater and exceeds 1.8 atoms for each atom of sodium. It is allowed to cool, the autoclave is opened, and the naphthalene is introduced. It is then heated to  $230^{\circ}$  to  $250^{\circ}$  at

10/20 kgm. of hydrogen pressure. The hydrogenation is completed at the end of two or three hours (the duration depends on the agitation).

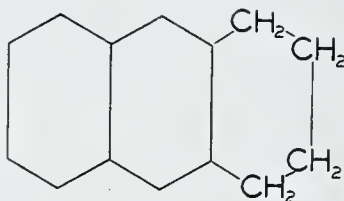
The tetralene coming out is colorless and contains a light gray powder in suspension, the sodium hydride. It is allowed to deposit and is then decanted. The catalyzer can be used again.

The hydrogenation of pure anthracene is, so to speak, startling. We were able to isolate exactly the same products as if nickel had been employed:

We observed first the formation of meso-di-hydro-anthracene:



The latter is transformed with subsequent quantities of hydrogen into 1-2-3-4 tetrahydroanthracene:



Then we have hexa and octo-hydro-anthracene. These different products can be prepared directly with a high degree of purity, if the hydrogenation is carried out with the necessary theoretical quantity of hydrogen.

Benzene cannot be hydrogenated in the presence of a hydride, neither can any of the derivatives that we have tested so far, which contain a benzene nucleus.

If the naphthalene can be hydrogenated quantitatively into tetralene, and not any further, must we not conclude with certain chemists who have arrived at the same conclusions by other ways, that the two nuclei of naphthalene are not identical, i.e., one is benzene-like, and the other is not? The latter only would be hydrogenizable in the presence of hydrogen.

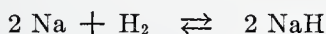
The hydrogenation of naphthalene into tetralene only is quite characteristic of sodium hydride. This is not the case with metals.

One might wonder why we do not use a metal, since a metal in the course of the hydrogenation process is, in any case, transformed into a hydride.

During the short period of existence of the metal hydride, it likewise causes hydrogenations, but the products are not necessarily the same as those formed in the presence of sodium hydride; in the case of naphthalene we obtain a certain quantity of decaline.

By introducing into the autoclave sodium and naphthalene that is heated to 230° to 250° under a hydrogen pressure of 10 to 20 kgm., a colorless liquid containing tetraline and a relatively small amount of decaline is produced. This liquid contains the hydride of sodium in suspension.

For this reason, it seems quite improbable to us, that the mechanism of the catalytic action of hydrides can be represented by the formula:



The hydride would give up, after this purification, its hydrogen to the organic matter, and the sodium would be retransformed into hydride under the influence of hydrogen pressure. We would thus have a cycle as is frequently accepted to be the case in catalytic reactions.

We incline rather toward the hypothesis of an activation of the hydrogen in contact with the hydride, perhaps, also an activation of the organic matter by the formation of unstable organo-metallic compounds.

The hydrides have another property which makes them especially valuable. Their catalytic power by no means suffers, from the presence of impurities and of poisons. There is at most the disappearance of a quantity of hydride equivalent to the impurities present.

Therefore, I suggest the use of these hydrogenation catalyzers for substances like tar, which cannot be purified.

The hydrogenation of pitch requires a hydrogen pressure of 80 to 100 kgm. and a temperature in the neighborhood of 300°. We have, accordingly, about the same conditions as those under which Staudinger hydrogenated rubber into hydrorubber with platinum as a catalyzer. These relatively high pressures are always necessary

when one works with colloidal substances. The amount of the catalyzer normally used is about 7 to 10 per cent.

Thus we obtain as the product of hydrogenation very green fluorescent oils in addition to an infusible, black, solid substance which swells very much upon being calcined. It has combined so firmly with the catalyzer that it is often difficult to prove the presence of the latter otherwise than by the total destruction of the organic matter. The yields in oil scarcely exceed 30 per cent under those conditions. We wished to know the cause of the formation of this product in order to try to prevent it, and to increase the yield in oils.

There are two facts concerning the composition of pitch that we do not know: first, the substances that enter into its composition, and second, the manner in which they are bound together to constitute the colloidal whole such as it is. It may be supposed that they are acid compounds, oxidized, sulphurized or nitrogenized, which enter into combination with the catalyzer and make it disappear and render it inactive.

It is certain that those substances are there for some reason. We saw, however, very quickly that it was much less the chemical structure than the colloidal physico-chemical constitution which was intervening.

According to Nellensteyn (*Chem. Weekl.*, 1927, vol. 24, p. 414) three substances may be distinguished as the constituents of asphalt: the oil medium, a lyophile part formed of protecting compounds, and a lyophote part formed by carbon.

The oily medium forms the external layer. The protecting compounds with the particles of carbon, form the asphalt micella in whose center the carbon is found. If we add to a similar medium a small quantity of any reagent whatsoever, (we studied three very different kinds, sodium hydride, sulphuric acid, and benzene), the reagent disappears, that is, it is absorbed.

If we add, on the other hand, a large quantity of the reagent, we notice an irreversible flocculation that is due to the destruction of the micella.

We treated pitch with variable quantities of boiling benzene, filtered it, and determined the residue insoluble in the benzene.

Normal benzene was added to the benzene solution; there appeared a red brown flocculent precipitate which we shall call solid bitumen. There also remains in the solution a product which appears after evaporation as a very thick oily liquid of red brown coloration. This is oily bitumen.

# EXTRACTION OF COAL TAR WITH BENZINE.

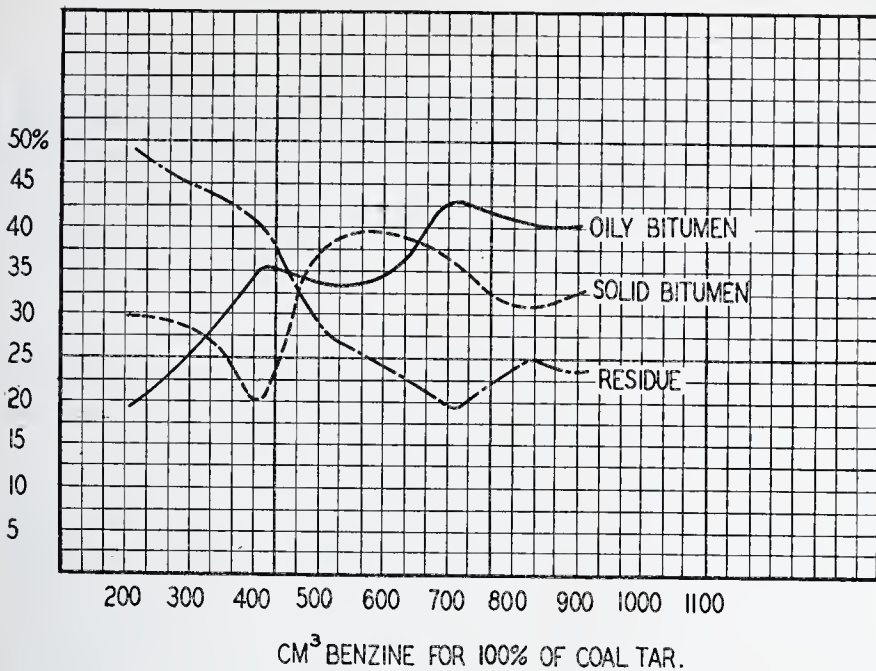


FIG. 1

The first curve (Fig. 1) represents the variation of the residue, the solid and the oily bitumens as a function of the quantity of benzene taken for the extraction. We see that these curves are absolutely irregular.

## EXTRACTION OF COAL TAR WITH 15% BENZINE ADDED BEFOREHAND

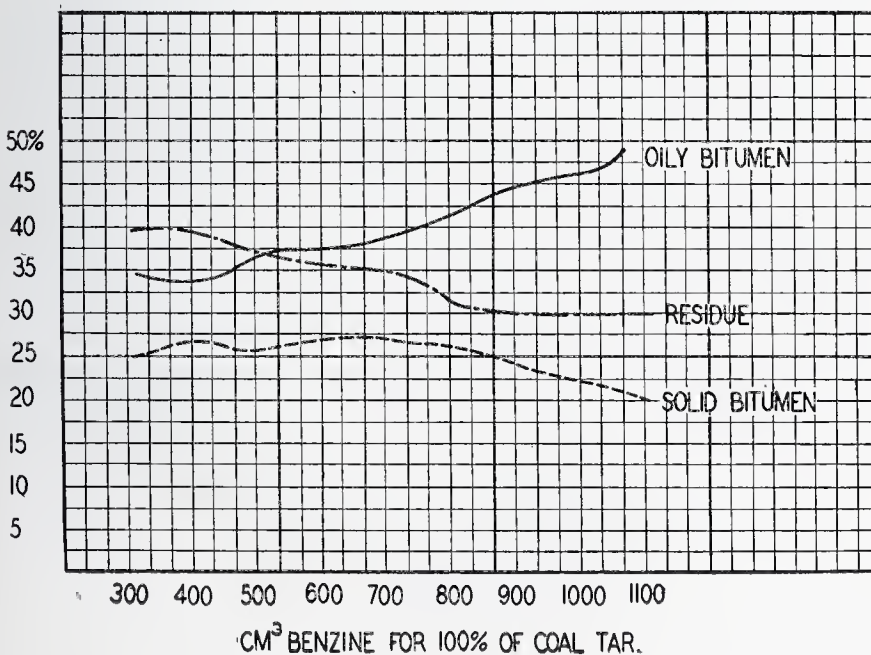


FIG. 2

The second curve (Fig. 2) represents the results obtained with a pitch to which we added beforehand 15 per cent by weight of benzene. It was then slowly heated to obtain a homogeneous mixture. The curves are more regular, they are almost straight. The quantity of insoluble matter in the benzene is considerably less, that of oily bitumen, much greater.

This shows very clearly the importance of the method of treating a pitch with a reagent. Even an operation which seems as simple as an extraction requires study, if we do not wish to be led to completely discordant results.

If considerable quantities of a reagent such as sodium hydride or sulphuric acid are added to the pitch, it appears evident that considerable proportions of oily or solid bitumen can be carried along in the flocculation. All that has flocculated is lost in the hydrogenation.

Guided by these considerations we were able to prevent this flocculation to a great degree, and we obtained, so far, yields of 80 per cent. If we take account of the fact that there is in this pitch about 5 per cent of carbon insoluble in any solvent, we find that the yield represents about 85 per cent of the organic substances of the pitch.

Let us see now how the transformation of pitch into oil is brought about. In carrying out the hydrogenation at a very low temperature, for example, 250° for pitch from a coking plant, we do not obtain oil. The result of this hydrogenation is a soft pitch which may be rather fluid, almost like a thick liquid. We must go beyond a certain temperature to obtain oils.

When we follow under favorable temperature conditions the successive transformations of the pitch as a function of the amount of hydrogen absorbed, we observe that the pitch absorbs the major part of the hydrogen without changing its colloidal constitution in any way. It becomes softer and softer until it finally becomes this viscous thick liquid of which we spoke just a moment ago. One of the characteristics of this liquid is, that it is insoluble in benzene while the oils, that result from it, are miscible in all proportions. We shall call this product "hydropitch," or in French, "hydrobrai."

The properties of "hydropitch" are summed up in the following table:

D 19.5°	1.16
Flash point	130°
Fire point	215°
Visc. Engler at 50°	3.5
Brown red liquid	

The transformation of this "hydropitch" into oils gives rise to a relatively slight absorption of hydrogen. The oils obtained from this "hydropitch" have the following properties:

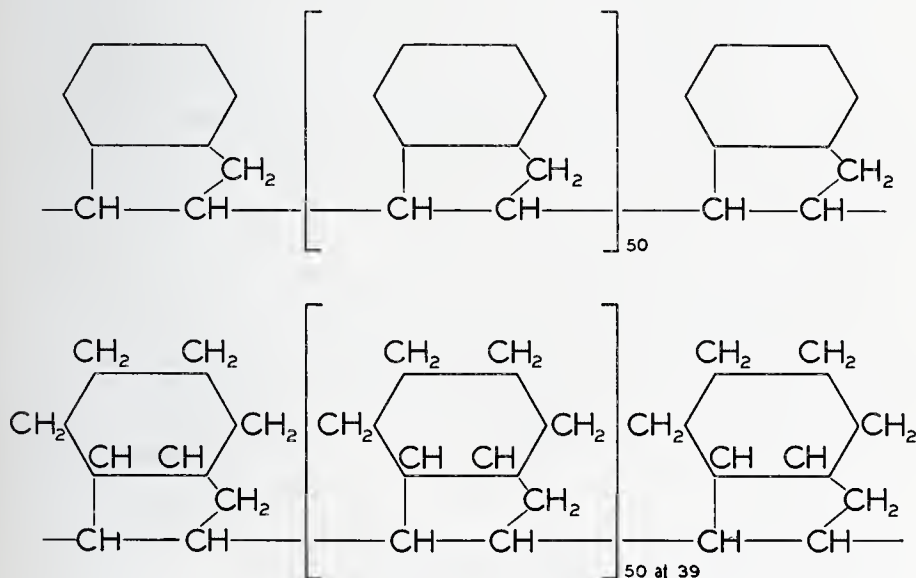
D 19°	1.06
Flash point	64°
Fire point	84°
Visc. Engler	{ 20° 10.4
	{ 50° 2.5
	{ 100° 1.3
Asphalt content	0.7 per cent
A very green fluorescent liquid	

The comparison of these two tables shows at once that the oils contain lighter products, more volatile than the "hydropitch."

The transformation of the "hydropitch" into oil consequently involves a cracking which destroys the colloidal structure of the "hydropitch." Parallel to this occurs another hydrogenation of the broken valences.

We have tried to picture these phenomena by taking substances with a known structure as models.

Let us suppose that we hydrogenate polymerized indene for which Staudinger proposes the following formula: (Staudinger, *Die Chemie der hochmolekularen organischen Stoffe im Sinne der Kekulischen Strukturlehre*, B. 59 (1926), p. 3019.)



This hydrogenation leads to a colloid hydrocarbon having the nature of cycloparaffin and a great stability. If we crack this hexahydropolyindene moderately we shall obtain smaller fragments which would saturate the free valences with hydrogen.

The first part, the transformation of polyindene into hexahydropolyindene would correspond to the passage of the pitch into "hydro-pitch" and it absorbs a large amount of hydrogen. The cracking of the hexahydropolyindene requires no more than a very small quantity of hydrogen.

We have been able to accomplish this, at least in part, by following the example of polystyrolene. We took vitreous polystyrolene and treated it with sodium hydride under hydrogen pressure at  $350^{\circ}$  (100 kgm.). The transformation into hexahydropolystyrolene was not possible because with our catalyzer the hydrogenation of the benzene nucleus was not realizable.

We were able to carry out only the second part of the operation, the cracking. Only a relatively slight amount of the hydrogen disappears. The result is a liquid which begins to boil at  $120^{\circ}$ . Judging from the various stages observed during the course of the distillation it contains, for the most part, toluene, ethylbenzene, and xylenes, and also substances having boiling points above  $300^{\circ}$  and containing at least two benzene nuclei connected by a chain in the manner of 1-4 diphenyl butane.

It is certain that we have in the pitch, above all, very condensed nuclei. The phenylic nucleus is found only in very slight quantities. Let us remember that by the destructive distillation of pitch, we obtain only traces of benzene, and that the naphthalenic nucleus and other polyaromatics are very difficult to crack, and do not enter again into consideration in the production of benzene. Our pitch oils contain practically no benzene.

The first products of distillation begin to pass at  $200^{\circ}$ , thus indicating the presence of tetraline, and consequently even the presence of the naphthalenic nucleus. The major part of the substances constituting these oils must contain extremely condensed nuclei, when we consider that they distill at ordinary pressure without decomposition, and moreover, at temperatures above  $500^{\circ}$  and even  $600^{\circ}$ . The base of these substances is certainly formed of polyaromatic hydrocarbons like chrysene, picene, and others, because by dehydrogenation well-crystallized hydrocarbons are produced.

These very condensed nuclei are bound together in the pitch like

those of polystyrolene by lateral non-saturated chains, or like those of polyindene by non-saturated hydroaromatic or cycloparaffinic nuclei.

In this hypothesis on the structure of pitch we have not considered its content in oxygen, in nitrogen and in sulphur. It is probable that these elements contribute very much to linking the different molecules together. Oxygen is, however, the chief content of the so-called free carbon portion, and thus belongs to the insoluble products of the pitch which are the most difficult to hydrogenize. The oxygen reacts with sodium hydride. The nitrogen is expelled in the form of ammonia. The sulphur is removed likewise in the form of sodium sulphide.

The deoxidation and desulphurization reactions occur very rapidly after the beginning of the hydrogenation. However, there seems to be no change in the colloidal structure of the pitch. We think that we are able to conclude that the colloidal structure of pitch is at least not due exclusively to oxygenated, nitrogenized or sulphurized unions, but in a great degree to a polymerization of the highly non-saturated carburetted linkages.

#### DISCUSSION

J. B. SHOHAN (United States Bureau of Mines, Pittsburgh, Pa.): I would like to ask if the ash was included in the calculation of the portions insoluble in phenol?

MR. GRAHAM: The results are all ash-free.

DR. T. E. LAYNG (University of Illinois, Urbana, Illinois): I would like to ask why you show phenol as your extracting solvent in preference to some other substance?

Have you tried extracting various types of wood? We have made some experiments at the University of Illinois using phenol as the extracting liquid.

In spite of very careful removal of the extracting liquid, the weight of the extract and the residue from some coals totals more than that of the coal treated. This is especially noticeable with coals of the lignitic type where an increase in weight of as much as 10 per cent is often obtained. With coals of the carbonaceous type the increase is much smaller while with woods we have obtained an increase of as much as 25 per cent. I should like to know whether you have obtained similar results.

MR. GRAHAM: We have not tried any experiments on wood. We believe that the residue is free from phenol, after our treatment, which involved washing with ether, then caustic soda solution and finally heating in vacuo at 100°C.

We have tried using pyridine, which is one of the other substances to which you refer, but the action of hydrogen on this gave piperidine and other compounds.

DR. FRIEDRICH BERGIUS (Heidelberg, Germany): It is very interesting to see that phenol as a distributing medium, as a solvent, as you may call it, gives a better hydrogenation action.

In the experiment I can see that most of the coals give more than 20 to 25 per cent of a solid residue, isn't that true?

MR. GRAHAM: Yes.

DR. BERGIUS: A lot of the products of coal containing about 80 per cent of carbon have certainly 40 per cent of solid residues.

If you take a set of phenols, and other solvents, as we did, especially the oil made out of coal, these figures are then much lower. In lignites, or brown coal, you come down to about 2 per cent if you use another solvent, and also for coals containing about 80 to 84 per cent of carbon we used to have about 10, 12 or 15 per cent of solid residues. We used to have it in hundreds of different experiments.

That means that the phenol must have a special chemical effect or reaction or that during the experiment the distribution of heat may not be quite correct. As I understand it, you took about two parts of coal and mixed it with one part of phenol, is that right?

MR. GRAHAM: That is right.

DR. BERGIUS: I cannot imagine that in such a mixture the whole system is liquid enough, and that superheating from the walls is not totally excluded. Such reaction being very sensitive to superheating something may occur, such as a sort of coking. You know perhaps that this reaction is more or less a competition between two reactions, the reaction of breaking up the coal molecule and the reaction of adding hydrogen into this broken-up molecule.

If temperature is a little too high the decomposition reaction rules the system and hydrogenation cannot take place easily and quickly enough. That is the great danger for such experiments.

I quite agree with Mr. Graham's statement about carbon content, the higher the carbon content is, the more residue remains. In 1916 a patent was taken out revealing this question, and saying that you should use especially for this purpose coal which contained less than 85 per cent of carbon. That was also the theoretical basis of our first experiments with the coal of the sort which we called end coal, according to our ideas of the coal formation, a question which I talked of yesterday, that these coals readily add hydrogen and that the coals containing higher percentages of hydrogen have suffered some change in nature perhaps due to the very high pressures of the mountain regions.

DR. SHOHAH: In the abstract of Mr. Graham's paper it is said, "The value of hydrogenation as a means of elucidating further the constitution of coal is emphasized."

I should like to ask Mr. Graham to what extent that is possible, inasmuch as coal at 450°C. certainly loses its original identity.

MR. GRAHAM: In reply to the last speaker I fully agree that what we are doing in the main is hydrogenating a product of decomposition. You have not got the coal in its original condition when you get up to a temperature of 430°C. It may be only a rearrangement of the molecules but I think that some change has taken place possibly by depolymerization of some of the coal molecules, if you like to put it that way, giving unsaturated bonds and the hydrogen has an opportunity of stepping in and producing hydrogenated products. The value of hydrogenation in elucidating the constitution of coal lies in what is more than a theory, I think, viz., that ease of hydrogenation depends largely upon the molecular structure of the compounds in coal or those which are produced when the coal is heated to 430°C.

We have carried out experiments in nitrogen, which showed a certain production of oil at the same temperature as that at which we carried out the hydrogenation experiments. But, the amount of oil produced is very much smaller, and the product is, as I mentioned, much less saturated, the iodine values being very much higher.

With reference to Dr. Bergius' remark about the proportion of coal to phenol, I did mention in the paper that we used originally one part of coal to two parts of phenol. Later we altered the proportion to two parts of coal to one of phenol, as that was the proportion which Dr. Bergius himself has employed. This quantity of phenol plus the oil produced is sufficient to keep the mass in the autoclave in a sufficiently fluid condition to ensure thorough mixing and no super-heating. I do not think that the lower yield which we have obtained is due so much to superheating in our experiments as to the combination of the higher pressure and the use of oxide of iron in Dr. Bergius' tests.

In general, I think our results have shown great similarity to those obtained by Dr. Bergius. If he had remained here I should have liked to ask him how far his oily product is really a true oil, and whether it does not contain some matter in colloidal suspension. The ash of our tar-oil has been determined and found to be practically negligible and I should like to ask Dr. Bergius if he has found the same in his oils, which have been obtained on a larger scale.

I pointed out in the paper that we have not included phenols in our results and that fact again would tend to make our results for oil yield lower than those of Dr. Bergius'.

DR. W. H. FULWEILER (U. G. I. Company, Philadelphia, Pa.): There are two questions that I should like to ask Dr. Arend. These concern the construction of the furnace and the method of determining the swelling.

DR. AREND: We use an electrical furnace in the middle of which there is a tube of quartz, having about 200 mm. of flanks. The quartz tube is in the

middle of the electrical furnace and the heating is very uniform. On the powdered coal we have a disk and a rod which is connected with a lever. So when you are heating you are swelling on a graduated scale and the results are always put on a diagram. It may be a relative scale, just as you like. For the expansion curve you have the increase of volume and for the other you always put the time. As you read the increase in volume every second you also get the increase in time.

DR. FULWEILER: What is the rate of heating? How many degrees per minute?

DR. AREND: We have seen temperatures varying from the different kinds of coal, between  $480^{\circ}$  and  $520^{\circ}$ . The maximum of heat employed is about  $550^{\circ}$ .

DR. FULWEILER: How fast do you heat? What is your rate of heating?

DR. AREND: I believe it is at the rate of  $20^{\circ}$  for each five minutes.

DR. FULWEILER: Do you not find the rate of heating making a difference in the curve?

DR. AREND: It makes no difference on the curve if you heat uniformly. In the experiments you must heat your furnace in the same way; that is where you get the thermic points. The characteristics of the curve is not changed. It changes your scale. You must always try to work with the same operator, or under as nearly the same condition as possible, in order to compare results.

CHAIRMAN HASLAM: As I recall experiments conducted back at the Massachusetts Institute of Technology several years ago, the rate of swelling in an apparatus similar to the one described is very materially influenced by the rate of heating. I cannot quite remember the exact data but I think on all the coal tried, which as I remember came from Westmoreland, from Illinois, some from the far west and so forth, that did hold.

DR. FULWEILER: We have tried a large number of American coals with a very similar method and we found that the shape of the curve, and the relative heights of the curve, are dependent on rate of heating, this is more marked when the rate is somewhat slower than the rate you mentioned. We would consider that five degrees per minute is fast. If the rate is lowered to one degree per minute then with some types of coal there is a decided change both in the shape and the relative heights of the curves. There is apparently time for an accelerated oxidation to take place.

In some coals even in an atmosphere of nitrogen there is a decomposition of some component of the coal which changes the swelling properties.

DR. C. H. GREENWALT (DuPont Company, Wilmington, Del.): I should like to ask Mr. Graham whether he has determined the effect of the rate of agitation on the rate of hydrogenation and the extent of hydrogenation?

I know in some experiments I have conducted on the rate of hydrogenation of other materials, the rate of agitation makes a tremendous difference up to a certain point. After passing a certain critical velocity, for instance there is not so much difference, but up to that velocity there is a great deal of difference.

I always thought that this effect was due to the rate of solubility of hydrogen in the liquid material to be hydrogenated and that the absorption of hydrogen by the solid, or liquid, material was quite rapid. The reason for agitating rapidly was to keep the liquid saturated with hydrogen.

I should, therefore, think the great many discrepancies on the extent and the rate of hydrogenation of coal might be due to differences in rate of agitation and intimacy of contact between the material to be hydrogenated and the hydrogen itself.

MR. GRAHAM: In reply to the last speaker, we have not tried any experiments on the rate of agitation. We have carried our experiments under the standard conditions, which have been rather forced upon us by the gearing of the autoclave. I cannot add anything more to that, I am afraid, beyond saying that the speed of rotation of the autoclave was quite sufficient to ensure thorough mixing of the contents.

DR. P. N. LATEGAN (Union of South Africa, Johannesburg): I would like to ask whether Mr. Graham does not think that the reaction taking place in this method of hydrogenation is not initially a solvent reaction and the process of distillation, with subsequent hydrogenation of the product, the heat product and the product of distillation?

The reason why he said it made no appreciable difference whether the experiment was carried out at a pressure of 150 or 250 probably is that.

MR. GRAHAM: There is not a great deal of difference.

DR. LATEGAN: That makes me think that you get this solvent action and you dissolve out a certain quantity of coal and it does not matter how high you take the pressure you can only get a certain yield of hydrogenation products.

MR. GRAHAM: The amount of phenol we use can hardly be looked on as a solvent for the coal. I do think it acts as a solvent for the hydrogenation products. Moreover our experiments indicate that the portions of coal which dissolve readily in phenol are not readily hydrogenated.

The experiments carried out with the coal in the absence of phenol showed the hydrogenation only proceeded to a certain stage. As far as we could see the products of hydrogenation tend to clog up the coal and prevent further action of hydrogen. By the use of phenol, I think those products are removed and the hydrogen has further opportunity of attacking the coal substance. As I explained before, I think the greater amount of hydrogenation is caused by a certain decomposition or depolymerization of the molecules forming the coal.

DR. GREENWALT: I should like to ask Mr. Graham whether the condition of 450°C. is above or below the critical temperature of the phenol? Is the phenol liquid under the conditions of his experiments?

MR. GRAHAM: Yes, that is so.

DR. SHOHAN: Mr. Graham stated he obtains a portion labelled P. which is soluble in phenol but not in chloroform. He said it might be a partially hydrogenated product. Has he carried on a further hydrogenation with that product or does he contemplate doing so?

MR. GRAHAM: We have not so far, but we contemplate doing so.

DR. SHOHAN: Has Mr. Graham hydrogenated the portion that is soluble in pyridine or only the residue?

MR. GRAHAM: Just the residue so far.

CHAIRMAN HASLAM: I would like to ask what the per cent of gas was that was formed when you hydrogenated the para-bituminous coals in 1920 and 1922? That is what is it on the ones that had the high conversion?

MR. GRAHAM: In the case of the first of those it was 14.6 per cent of gas.

CHAIRMAN HASLAM: That is based on weight?

MR. GRAHAM: The "ash-per-dry" weight. In the case of 20 there was a rather smaller amount, only 8.9. In 21 it was 15.20 per cent, and then in 22 it was 17.0.

DR. C. R. DOWNS (Weiss & Downs, New York, N. Y.): Concerning heating the coal, in showing the rate at which the swelling takes place, anybody who has handled coal knows that if you hold a plunger in the cylinder you can feel the material puff up. When you reach that point at which the greatest swelling is taking place, according to your conclusions, as I understand them, that is the point at which hydrogenation should be carried out.

If catalysts promote hydrogenation of coal does the presence of the catalyst affect the temperature at which maximum swelling takes place, or is it an activation of the hydrogen gas to make it hydrogenate the decomposition product of the coal. In other words, have you tried mixing catalysts with your coal and heating it up to note whether the velocity of swelling has been changed or whether it is merely an effect upon the hydrogen to make the gas more active for hydrogenation?

DR. AREND: This question has not been clear, because up till now this has been the work of the research laboratories and the work is not yet finished. I cannot give you a clear answer to the question.

DR. DOWNS: This apparatus as I understand it is on the principle of Les-sing's tube, in which he used a quartz tube and a quartz plunger inside the tube. A certain weight of coal in the tube was placed in a furnace at a given temperature and the heat inflow into the tube depended on the diameter of the tube and the amount of coal present. In the same way each determination on your curve was a separate determination and not a continual curve derived from one sample of coal; was it not?

DR. AREND: That is so. The highest point of the curve is always the same because the velocity you have gives another scale, but individual forms are there and the inclination is to remain the same. That is, however, another scale.

DR. LATEGAN: I would like to ask Mr. Graham what percentage of the "B" product he gets in his blank experiments?

MR. GRAHAM: I am glad the question was asked. I am afraid I did not mention it in this paper.

We get practically no "B" product at all in the blank experiments. That product is definitely one of hydrogenation. In that respect it is of great interest to us as we feel we have insolated a product produced by the partial hydrogenation of the coal. Whether we can convert that by further hydrogenation into oil is a matter which we have to determine.

# A CONTRIBUTION TO THE STUDY OF THE SYNTHESIS OF METHYL ALCOHOL

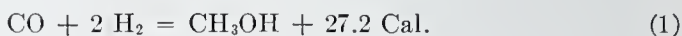
By E. AUDIBERT

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The French National Society for Research on the Treatment of Fuels has undertaken, among other studies, that of the manufacture of methyl alcohol from mixtures of carbon monoxide and hydrogen. I propose in the following paper to review briefly the results obtained in this work up to the present time. I must, however, point out that this description will remain incomplete, and that I will not be able to draw any definite conclusions from this work. The reason is that, at the time this paper was prepared, the different branches of research composing our program were not all completed.

The following chemical reaction:



which results in the formation of methyl alcohol, takes place under pressures varying from 10 or more to several hundred atmospheres, and at temperatures between 350° and 930°F., in the presence of a large number of solids. Among the latter, those which present a catalytic power sufficient to adapt them to the industrial manufacture of synthetic alcohol, contain either zinc oxide or metallic copper obtained by the reduction by hydrogen of the black oxide precipitated at boiling temperature by soda from a solution containing, among other compounds, a soluble copper salt. These catalyzers can therefore be divided into two classes; both of these are subject to a peculiar phenomenon which, for sake of simplicity, I will call "fouling."

A brief discussion of this phenomenon will be useful:

## 1. THE FOULING OF CATALYZERS

When a mixture of strictly pure carbon monoxide and hydrogen, in constant proportions, has circulated for a certain time over a catalyzer such as those used in the synthesis of methyl alcohol, while the pressure, the temperature distribution throughout the catalyzer

volume, and the rate of flow of the gaseous mixture are maintained constant, there is observed a gradual reduction, in some cases extremely slow, in the alcohol yield per unit of time. This reduction may be due to two distinct causes: (1) a physical transformation of the catalyzer under the action of heat, which will be studied later, and (2) the phenomenon indicated above as "fouling."

This action is due to the fact that certain compounds of higher molecular weight than methyl alcohol are formed simultaneously with it, though in infinitely smaller quantities—so much smaller indeed that it is extremely difficult to detect their presence in the liquid produced. Some of these compounds, only partly vaporized, remain fixed to the surface of the catalyzer, which they gradually cover. They may be detected by treating the catalyzer with nitric acid; the reaction leaves a black solid residue that contains a high proportion of carbon.

The partial pressure of carbon monoxide in the vapor phase is the dominant factor upon which depends the rate of fouling of the catalyzer. For instance, using the same copper-base catalyzer which we had kept in service for 6 hours under a total pressure of 150 atmospheres, the residue of the attack by nitric acid contained the following proportions of carbon: 0.135 per cent of the total weight, when the gaseous mixture under treatment consisted of  $\text{CO} + \text{H}_2$ ; unappreciable traces, when the gaseous mixture was  $\text{CO} + 5\text{H}_2$ .

Both the copper and zinc oxide catalyzers are subject to the process of fouling described above. For the same partial pressure of carbon monoxide, it is more rapid with the most active copper-base than for the most active zinc oxide catalyzers. However, this is probably related to the fact that, under identical conditions, the first class of catalyzers give a rate of production of methyl alcohol and therefore of activation of carbon monoxide, three or four times higher than the rate attainable with zinc oxide catalyzers. It is my belief that, when the two classes of catalyzers function under conditions giving the same hourly yield of alcohol per unit of catalyzer volume, the rates of fouling of the two classes will be of the same order of magnitude. However this fact has not yet been brought out with sufficient accuracy to justify a positive assertion.

At all events, in a test approximating the length of ordinary laboratory experiments, the effects of fouling are practically unappreciable when the partial pressures of carbon monoxide do not exceed 50 atmospheres, in the presence of the best zinc oxide base catalyzers, and 25 atmospheres in the presence of the best copper-base catalyzers.

For this reason, in the experiments described below, where the total pressures did not exceed 150 to 200 atmospheres, the following gaseous mixtures were used:  $\text{CO} + 5 \text{H}_2$  with copper-base catalyzers;  $\text{CO} + 5 \text{H}_2$  or  $\text{CO} + 2 \text{H}_2$  with zinc oxide base catalyzers.

By this expedient, the experimental results are not materially affected by fouling of the catalyzer. I cannot say, however, whether it actually results in the radical prevention of the formation of heavy molecules capable of adhering to the catalyzers, or merely reduces the rate of this phenomenon below the limit of sensitiveness of the methods of measurement used to investigate it.

In fact, we had occasion to observe that copper-base catalyzers which were completely soluble in nitric acid, after about 50 hours of operation in a mixture of pure gases consisting of  $\text{CO} + 5 \text{H}_2$ , at a pressure of 150 atmospheres, are no longer completely soluble after 300 to 400 hours of operation in a mixture of the same proportions of industrial gases. But we have not yet determined whether the polymerization resulting in the formation of the insoluble residue, which amounted to approximately 0.15 per cent of the weight of the catalyzer, took place at the expense of the carbon monoxide alone, or also at the expense of carbonaceous impurities which might exist in unmeasurable proportions in the initial mixtures of industrial gases, depending on the method used to prepare this mixture.

## 2. METHOD OF INVESTIGATION

After the foregoing indications regarding catalyzer fouling, it may be useful, before proceeding with the discussion of the properties of the catalyzers used in the synthesis of methyl alcohol, to outline the experimental methods used in this investigation.

When a gaseous mixture capable of undergoing an exothermal reaction in the presence of a catalyzer flows through a given catalyzer tube, under conditions of strictly constant flow and pressure, the rate of formation of the product of the reaction varies with the temperature of the gaseous mixture at the inlet of the catalyzer volume. Furthermore, for the same inlet temperature, the rate of the reaction varies when the arrangement of the catalyzer volume is changed, the influence of this factor being due to the fact that the temperature régime within the catalyzer volume is dependent on conditions affecting the dissipation of the heat generated by the reaction.

In order to make possible a comparison of results obtained under different operating conditions, the equipment used in these experi-

ments was arranged to dissipate the heat generated at the contact of the catalyzer at a rate sufficient to reduce to 36°F. the maximum temperature difference existing in the catalyzer volume. Under these conditions, the temperature at the geometric center of the catalyzer volume constitutes a datum that is not lacking in physical meaning, and that I have adopted as the "temperature of the catalyzer." When the gaseous mixture is kept constant, together with the total pressure and the rate of flow,<sup>1</sup> through the catalyzer volume, the hourly yield per unit of catalyzer volume is a function of the catalyzer temperature. This function, which is nil for all temperatures below a certain temperature, first increases with the temperature, then passes through a maximum beyond which it decreases. This maximum point is a convenient characteristic of the operating régime defined by the nature of the catalyzer, the composition of the gases, their temperature and the yield.

### 3. ACTION OF HEAT ON THE CATALYZERS

It is known that the properties of numerous catalyzers, when subjected for a sufficient length of time to a sufficiently high temperature, undergo a change which reduces their activity. Copper prepared by reduction of its oxide, zinc oxide, and the different catalyzers used for the synthesis of methyl alcohol which can be prepared from one or the other of these two products, are no exceptions to this law. Other things being equal, their activity varies inversely with the time of exposure to the high temperature and with the value of this temperature.

For instance, for the maximum hourly yield of methyl alcohol per cubic foot of catalytic volume, corresponding to a gaseous mixture of  $\text{CO} + 5 \text{H}_2$  at a pressure of 150 atmospheres and a rate of flow of 5000 feet per hour, we have measured the following yields:

- (260 grams) 16.2 pounds per cubic foot, when the catalyzer consisted of freshly-reduced copper;
- (200 grams) 12.5 pounds per cubic foot with the same catalyzer after exposure of the latter for 6 hours to a temperature of (450°C.) 840°F. in an atmosphere of hydrogen;

<sup>1</sup> We have adopted as a measure of the rate of flow of the gaseous mixture through the catalytic volume, the number of cubic feet N.T.P. of this mixture brought into contact with the catalyzer per hour and per cubic foot of catalyzer volume. This value I will call the rate of flow.

- (170 grams) 10.6 pounds per cubic foot with the same catalyzer after exposure of the latter for 6 hours to a temperature of (550°C.) 1020°F. in an atmosphere of hydrogen;
- (210 grams) 13.1 pounds per cubic foot when the catalyzer consisted of freshly precipitated zinc hydrate;
- (155 grams) 9.67 pounds per cubic foot with the same catalyzer, after exposure of the latter for 6 hours to a temperature of (450°C.) 840°F. in an atmosphere of hydrogen;
- (90 grams) 5.62 pounds per cubic foot with the same catalyzer, after exposure of the latter for 6 hours to a temperature of (550°C.) 1020°F. in an atmosphere of hydrogen.

As already noted in similar cases by previous investigators, we also had occasions to observe that the reduction in catalytic activity evidenced by the foregoing figures is related to the growth of the crystalline structure of the catalyzer. The x-ray spectrum of a freshly prepared catalyzer contains only a very small number of the characteristic lines of the substance. In fact these few lines are barely visible. After a six hour treatment at (450°C.) 840°F. or (550°C.) 1020°F., the same sample gives, on the contrary, under the same conditions of exposure, a spectrum comprising considerably clearer lines, and visible in much larger numbers.

#### 4. PROMOTERS

It has been observed in a large number of cases of catalysis that the addition to the catalyzer of one or more foreign products, whether these products possess catalytic properties or not, has the effect of modifying not only the activity of the catalyzer, but the effect of heat on this factor. The influence of the "promoter" (as this class of products has been called, to distinguish them from the catalyzer proper) may be favorable or unfavorable, depending on the nature and the quantity of the promoter used.

The phenomenon is found in the synthesis of methyl alcohol, both with reduced copper and with zinc oxide. It does not present identically the same character in both cases, however. Whereas the properties of a copper catalyzer are frequently varied between wide limits by the addition of extremely small proportions of certain promoters, those of zinc oxide usually vary slowly with the proportions of promoters.

In order to illustrate the action of promoters, which is so irregular and capricious that it defies all hard and fast definition, I will give below a few of the results obtained in our study of the variations in the catalytic properties resulting from the addition of different metallic oxides, reducible or not.

The oxides of tin and of bismuth, even in very small amounts, of the order of one atom to twenty of the metallic bases, have the effect of completely paralyzing reduced copper, which loses all power to catalyze the synthesis of methyl alcohol. The oxides of boron, titanium and vanadium, on the contrary, have practically no effect on the catalytic activity of freshly-reduced copper, but materially accelerate the rate of loss of activity under the influence of heat. Other oxides increase both the initial catalytic activity of reduced copper, and its resistance to the unfavorable action of heat.

As an example of the last case, we have obtained, under the following conditions:

A gaseous mixture composed of  $\text{CO} + 5 \text{H}_2$ ,

A rate of gas flow of 5000 cubic feet per hour per cubic foot of catalyzer volume,

A pressure of 150 atmospheres,

the following yields respectively with freshly-prepared catalyzers, and with catalyzers previously subjected for 6 hours to a temperature of  $(450^\circ\text{C.})$   $840^\circ\text{F.}$ , in an atmosphere of hydrogen:

(825 and 630 grams) 51.6 and 39.3 pounds per cubic foot when the contact substance was prepared by reduction from a mixture of copper and aluminum oxides, in the proportion of one atom of aluminum for 100 atoms of copper: (1070 and 975 grams) 66.8 and 60.8 pounds per cubic foot when the contact substance was prepared by reduction from a mixture of copper and cerium oxides, in the proportion of 1 atom of cerium per 100 of copper.

These figures show an increase over those obtained with copper alone of the order of:

215 per cent for the mixture of copper and aluminum,

310 per cent and 385 per cent for the mixture of copper and cerium.

With zinc oxide, the addition of other metallic oxides may be unfavorable, as in the case of tungsten oxides, indifferent, as in the case of uranium oxide, favorable, as in the case of glucinium oxide and chromium sesquioxide.

The foregoing indications give an idea of the function of the products added to the basic catalyzer. However, this factor is not

the only one upon which depend the results; the quantities of the promoters used, also their method of preparation influence the results closely. For instance, the maximum hourly yields per unit of catalyzer volume recorded, under the conditions outlined above, in the presence of metallic copper and of manganous oxide, are respectively:

(585 and 170 grams per liter) 36.5 and 10.6 pounds per cubic foot, with a catalyzing mixture composed of 1.25 atoms of manganese per one of copper; (970 and 0 grams per liter) 60.5 and 0 pounds per cubic foot with a catalyzing mixture composed of 2.5 atoms of manganese per one of copper.

As an example of the effect of the method used to prepare the catalyzing mixture, a given mixture of zinc oxide and sesquioxide of chromium gives notably different results if prepared by precipitating a mixture of nitrates with soda, or by reducing a chromate.

In closing the discussion of the influence of the nature of the catalyzer in the synthesis of methyl alcohol, it may be said that, on the whole, copper-base catalyzers seem considerably more active than those with a zinc oxide base. This will appear from the following characteristics which are those of the mixtures giving the best results of all those investigated in both classes.

With copper-base catalyzers, using a gaseous mixture of  $\text{CO} + 5 \text{H}_2$  (the only mixture studied in this case, for the reasons indicated in No. 1), under a pressure of 150 atmospheres and at a rate of flow of 5000, the hourly yields observed were of the order of (1100 to 1150 grams of alcohol per liter of catalytic volume) 69 to 72 pounds of alcohol per cubic foot of catalyzer volume. These yields are obtained at temperatures of the catalyzer that do not usually exceed values of the order of ( $275^\circ\text{C}.$ )  $530^\circ\text{F}.$

With zinc oxide catalyzers, which in our investigations were studied in connection with gaseous mixtures consisting of  $\text{CO} + 2 \text{H}_2$ , this mixture giving the best results, as was mentioned above, the hourly yield, under the same conditions of pressure and rate of flow as in the preceding case, never exceeded values of the order of (300 to 325 grams per liter of catalyzer volume) 19 to 22 pounds of alcohol per cubic foot of catalyzer volume. The temperature corresponding to the maximum of these values is, in this case, of the order of ( $375^\circ\text{C}.$ )  $700^\circ\text{F}.$

In both cases, the yield is not materially affected by the previous exposure of the catalyzer to a temperature of ( $550^\circ\text{C}.$ )  $1020^\circ\text{F}.$  in an atmosphere of hydrogen.

## 5. ACTION OF PRESSURE

When the composition of the gaseous mixture and its rate of flow are maintained constant, the maximum hourly yield  $R$  per unit of catalytic volume increases with the working pressure  $P$ . If a rather rough approximation be acceptable, it may be admitted that the yield is about proportional to the square of the pressure.

With a gaseous mixture consisting of  $\text{CO} + 5 \text{H}_2$ , and a rate of flow of 5000, we found that the best copper-base catalyzers give hourly yields which vary only slightly from the formula

$$R = 0.00312 P^2*$$

\* In metric units, with  $R$  expressed in grams of alcohol per liter of catalyzer volume and  $P$  in atmospheres, the relation is  $R = 0.050 P^2$ .

where  $R$  = yield of alcohol per unit of catalyzer volume, in pounds per cubic foot,

$P$  = absolute pressure of gaseous mixture, in atmospheres.

With a gaseous mixture consisting of  $\text{CO} + 2 \text{H}_2$ , and the same rate of flow of 5000, the best catalyzers with a zinc oxide base give yields that approximate the relation

$$R = 0.000874 P^2*$$

\* In metric units, this relation is  $R = 0.014 P^2$  where  $R$  = yield in grams per liter of catalyzer volume.

where  $R$  = yield of alcohol in pounds per cubic foot of catalyzer volume

$P$  = pressure of gaseous mixture, in atmospheres.

From these relations, it may be seen that, to reach the same hourly yield of alcohol with the same rate of flow, through the catalyzer volume, the pressures necessary with zinc oxide catalyzers must be about 90 per cent higher than those necessary with copper catalyzers.

In accordance with a general law, the temperature corresponding to a maximum yield increases as a function of the pressure. For instance, with the best zinc oxide catalyzers, the temperature rises about  $55^\circ$  ( $30^\circ\text{C}.$ ) when the working pressure rises from 150 to 400 atmospheres.

## 6. INFLUENCE OF THE COMPOSITION OF THE GASEOUS MIXTURE

For given values of the operating pressure and of the rate of flow, the maximum hourly yield obtained with zinc oxide catalyzers increases as the gaseous mixture approaches the composition  $\text{CO} +$

2 H<sub>2</sub>. Thus, under a pressure of 150 atmospheres and at a rate of flow of 5000, a catalyzer capable of producing (about 320 grams of alcohol per liter per hour) about 20 pounds of alcohol per liter per hour; with a gaseous mixture of CO + 2 H<sub>2</sub>, gives lower yields when an excess of either of the two gases is added in the gaseous phase; mixtures of CO + H<sub>2</sub> and CO + 5 H<sub>2</sub> do not, under the same conditions, give maximum yields exceeding (250 grams per liter per hour) 15.6 pounds per cubic foot per hour.

In view of these results, on the one hand, and of the precautions to be observed to avoid catalyzer fouling on the other hand, it has not appeared interesting to determine the behavior of copper-base catalyzers with gaseous mixtures varying from the composition CO + 5 H<sub>2</sub>.

## 7. INFLUENCE OF RATE OF FLOW

Other factors being equal, the hourly yield of alcohol varies in the same direction as the rate of flow, that is, in the opposite direction from the period of contact between the gas and the catalyzer. This is the direct consequence of the fact that the curve representing the proportion of methyl alcohol contained in the gases circulating through the catalyzer volume is convex towards the positive ordinates. As an example to visualize the nature of the relations between the quantities under consideration, I may give the following results, supplied by our investigation of a zinc oxide catalyzer:

Under the following conditions:

Pressure of the gaseous mixture = 150 atmospheres

Working temperature = (400°C.) 750°F.

Composition of gaseous mixture = CO + 2 H<sub>2</sub>,

we observe increases in the hourly yield per unit of catalyzer volume of approximately:

90 per cent when the rate of flow increased from 2,500 to 5,000,

55 per cent when the rate of flow increased from 5,000 to 10,000,

35 per cent when the rate of flow increased from 10,000 to 20,000.

## 8. CATALYZER POISONS

Copper-base catalyzers are incomparably more sensitive than zinc oxide base catalyzers, to the action of certain impurities in the surrounding atmosphere, and among those, to compounds of sulphur. This result is in perfect harmony with data secured from research concerning other reactions covering the intoxication of catalyzers. The following indication will serve to crystallize this effect:

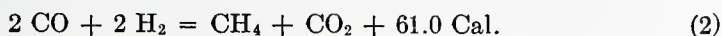
We treated in the presence of a copper-base catalyzer, under a pressure of 75 atmospheres, at a temperature of (275°C.) 525°F. and a rate of flow of 2500, a gaseous mixture of  $\text{CO} + 5 \text{H}_2$  containing, per cubic foot, 5.7 mgm. of sulphur, either as thiophene or as carbon bisulphide. In both cases, we recorded a rapid and continuous decrease in the activity of the catalyzer, without any corresponding change in other factors. The gas charged with thiophene lost all of its sulphur in the catalyzer volume, and left the apparatus perfectly pure; the catalyzer had lost all its activity after having fixed in this manner a quantity of thiophene corresponding to  $12 \times 10^{-3}$  atoms of sulphur for one atom of copper. The gas charged with carbon bisulphide, on the contrary, gave up only about half of its sulphur content to the catalyzer, and the catalyzer had lost all its activity only after having fixed about  $24 \times 10^{-3}$  atoms of sulphur per atom of copper. Therefore the catalyzer was put out of service about four times as fast in the first as in the second case, practically, in 7 hours of operation with thiophene and 30 hours with carbon bisulphide.

In another test, we operated during about 50 hours three tubes each containing the same zinc oxide catalyzer, and working under identical conditions: gaseous mixture  $\text{CO} + 5 \text{H}_2$ , 350 atmospheres, 400°C., rate of flow 12,000. The gas fed into the apparatus was pure for one tube, contained 5.7 mgm. of sulphur per cubic foot, as thiophene, for the second tube, and 5.7 mgm. of sulphur per cubic foot, as carbon bisulphide, for the third tube. After 50 hours of operation, the three tubes still gave exactly the same yield, as if the catalyzer had remained insensible to the impurities.

## 9. PARASITIC REACTIONS IN THE SYNTHESIS OF METHYL ALCOHOL

I had occasion in No. 1 to call attention to the fact that products of higher molecular weight than methyl alcohol may be formed simultaneously with the latter at the contact of the catalyzers. However, the reactions from which they result are not the only parasites of the principal reaction. It has been proved that others take place regularly. These may be classed in three distinct series, as follows:

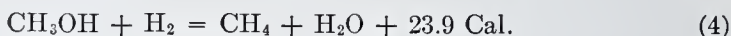
1. The combination of carbon monoxide and hydrogen to form methane and carbon dioxide, according to formula<sup>f</sup> (2);



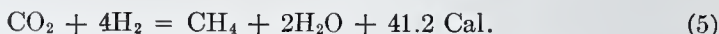
2. The decomposition of the alcohol produced in the principal reaction, according to formula (3)



or the reduction of the alcohol according to formula (4)



3. The reduction of the carbon dioxide formed in reactions (2) and (3) according to formula (5)



The following series of facts prove that the above reactions actually take place:

1. When a mixture of *pure* carbon monoxide and hydrogen, under pressure and temperature conditions favorable to reaction (1), flows at a sufficient rate over a catalyzer, of the kind used in the synthesis of methyl alcohol, the gas leaving the catalyzer volume is found to contain equal volumes of methane and of carbon dioxide. This is the proof that reaction (2) takes place simultaneously with reaction (1) in the presence of the catalyzer.

2. Let us assume a given quantity of catalyzer of reaction (1), contained in a closed vessel equipped with an appropriate device to maintain it at a constant temperature. Let us further assume that, after a vacuum has been created in this vessel, a mixture of pure carbon monoxide and hydrogen be suddenly admitted into this vessel, under a suitable pressure, and measurements be subsequently made to determine the variations in the composition of the gaseous phase in contact with the catalyzer at a constant temperature. If curves be plotted representing as functions of time the variations of the following ratios:

$R_M$  = the fraction of the original amount of carbon monoxide the carbon content of which is recovered as methyl alcohol;

$R_E$  = the fraction of the original amount of carbon monoxide the carbon content of which is recovered as carbon dioxide;

$R_W$  = the fraction of the original amount of carbon monoxide the carbon content of which is recovered as water.

Curve  $R_M$  rises rapidly from the origin and passes through a maximum beyond which the function decreases, approaching zero as an asymptote.

Curve  $R_E$  has the same general aspect, but rises more slowly from the origin, reaches its maximum point later, and its asymptote is not necessarily zero; this asymptote becomes zero only for sufficiently high values of temperature and pressure.

Curve  $R_W$  increases continually, but rises much more slowly from the origin than the two preceding curves.

These relations prove:

First, that the methyl alcohol formed at the contact of the catalyzer subsequently disappears gradually, undergoing at least one of the transformations represented by equations (3) and (4).

Secondly, that the carbon dioxide contained in the atmosphere surrounding the catalyzer is reduced, at least in part, in accordance with equation (5).

The development of the parasitic reactions defined above leads in any event to two important consequences, to wit:

1. The complete conversion of all the gaseous mixture into methyl alcohol is impossible, and a certain loss of the raw products of the process is inevitable.

From the viewpoint of practical applications, it is important to secure as precise a knowledge as possible regarding this point; that is to clearly define the influence of the different factors affecting the efficiency of utilization of the gas consumed by the process. Without undertaking a detailed analysis of the rôle of these factors, I wish to indicate the precautions to be observed to improve the efficiency of the transformation:

a. The methyl alcohol produced must be condensed before it has had a chance to remain long in contact with the catalyzer through which it has been formed;

b. It is advantageous to use a catalyzer as active as possible, and operating at the lowest possible temperature.

The first of these two conditions rests upon the fact that methyl alcohol is only an intermediate product in the transformation of the raw products in contact with the catalyzer, and that it is only by surprise so to speak, that it can be produced. The second condition rests upon the fact that the working temperature is the dominant factor in the speed of the parasitic reactions.

The result of the above conditions is that copper-base catalyzers are more advantageous than zinc oxide catalyzers, insofar as concerns the efficiency of utilization of the raw product. The following example, although purely theoretical, will serve to illustrate this point:

Let us assume, for the sake of simplicity, that reactions (1) and (2) alone take place, reactions (3), (4) and (5) being excluded; and let us consider the case where the catalyzer tube of the apparatus, arranged to maintain a practically constant temperature throughout the catalyzer volume, is included in a closed circuit in which the mixture of carbon monoxide and hydrogen flows at the rate of 5,000 cubic feet per hour per cubic foot of catalyzer volume. The experimental data which we have collected regarding the relative velocities of reactions (1) and (2) enable us to estimate that, when the temperature of the catalyzer volume corresponds to the maximum yield, the efficiency of utilization of the carbon monoxide reaches the values shown in Table I.

TABLE I

BASE OF CATALYZER	COP- PER	COP- PER	Zn O	Zn O	Zn O	Zn O
Partial pressure of mixture of carbon monoxide and hydrogen, atmospheres.....	150	150	150	150	400	400
Volumetric ratio of hydrogen to carbon monoxide.....	5	5	2	2	2	2
Proportion of impurities in the catalytic circuit.....	1/2	1/3	1/2	1/3	1/2	1/3
Working pressure, atmospheres.....	300	225	300	225	800	600
Efficiency of utilization of the carbon monoxide, per cent.....	95	95	65	60	69	66

From this table, the catalyzers based on zinc oxide do not allow more than two-thirds of the carbon monoxide to be transformed into methyl alcohol, whereas the copper-base catalyzers convert 95 per cent. This difference is still more marked when the temperature in the catalyzer volume rises above that corresponding to its maximum yield. For instance, when the temperature exceeds the most favorable value by (25°C.) 45°F., the efficiency of utilization drops to:

90 per cent with copper-base catalyzers, when the effective pressure is 150 atmospheres;

45 or 55 per cent with zinc oxide catalyzers, depending on whether the effective pressure is 150 or 400 atmospheres.

2. The development of the parasitic reactions has considerable influence in another way on the conditions of thermal operation of the catalyzing apparatus. Not only does it cause an increase, that may be considerable, in the quantity of heat generated per unit of

weight of the raw product consumed, but it also has the following disadvantage:

The adiabatic operation of a catalyzer in the presence of which takes place a reaction accompanied by the generation of heat and a reduction of volume does not allow the temperatures in the catalyzer volume to exceed a maximum, the value of which varies in the same direction as the pressure; this is the direct consequence of the fact that the inverse reaction causes absorption of heat. In the case of the synthesis of methyl alcohol, for example, the maximum temperature attainable in the catalyzer volume is about 180°F. above the initial temperature of the gas, when the working pressure is of the order of 150 atmospheres. Therefore, if there were no parasitic reactions, an installation treating under 150 atmospheres a mixture of carbon monoxide and hydrogen preheated to 500° or 550°F., would run no risk whatever that its internal temperature would ever rise above values of the order of 650° to 750°F.; and whatever precautions were taken to dissipate the heat generated by the reactor, there would be no danger either of an excessive reduction of the mechanical strength of the metal walls of the enclosure subjected to the working pressure, or of too rapid a growth of the crystalline structure of the catalyzer.

Conditions are entirely different when reactions (2) and (5) take place simultaneously with the principal reaction: At the pressure of 150 atmospheres, the maximum temperature which cannot be exceeded owing to the adiabatic development of the two parasitic reactions is of the order of (1500°C.) 2700°F., and until this temperature is reached, the reverse reactions will not come into play to limit the temperature rise due to the heat generated. Therefore, owing solely to these parasitic reactions, a tube containing a catalyzer of the synthesis of methyl alcohol, if operating adiabatically, would produce alcohol only at the beginning of its operation, and, after a certain time, would no longer yield anything but methane and water. Furthermore, the temperature would tend towards values under which metals lose very nearly all their mechanical strength.

The development of the parasitic reactions therefore precluded all possibility of automatically limiting the maximum temperature attainable, simply through the automatic reversal of the principal reaction. The apparatus must therefore be provided with sufficient means to evacuate the heat generated by the reactions. Any deficiency in heat-conveying capacity, any interruption of the cool-

ing action may lead to a rapid rise in the temperature, to the gradual distortion of the reactions in progress in the apparatus, and, at the last, to the probable explosion of the enclosing walls under the large operating pressures.

It may be useful to emphasize that the obstacles resulting from the development of the parasitic reactions, that is, the phenomenon of auto-intoxication discussed in No. 1, the loss of raw material and the danger of overheating discussed above, and which constitute a very marked difference between the synthesis of methyl alcohol and that of ammonia, are due, in final analysis, to the fact that the three elements to be combined, carbon, hydrogen and oxygen, may form an infinite number of different products, besides methyl alcohol. It is a question whether the synthesis of all organic compounds will not present peculiarities of the same kind.

#### CONCLUSION

On the whole, the research work of our laboratory indicates two different formulae for the manufacture of methyl alcohol:

One makes use of a rugged, though rather slow, catalyzer, which will function under pressures of several hundred atmospheres, probably of the order of 400 to 500. This method may be used with a gaseous mixture imperfectly purified, but with a mediocre efficiency. It also presents considerable risk of overheating of the catalyzer volume.

The second formula makes use of a much more active catalyzer, capable of operating under much lower pressures, and a materially lower temperature, but infinitely more sensitive to the effect of poisons. For this reason, it can only be used with a gaseous mixture much more carefully purified than in the former case. On the other hand, the efficiency of this method is much higher than that of the former, and the risk of overheating is much lower.

Whether the first or the second method will give the soundest foundation for the development of an industrial process is a problem that cannot be solved otherwise than by further experiments on a semi-industrial scale. These have been undertaken by the "Société Nationale de Recherches," but were not yet sufficiently advanced at the time the present paper was prepared, to afford a basis for any definite conclusions.

# HYDROGENATION AT HIGH PRESSURE AND HIGH TEMPERATURE WITH OR WITHOUT CATALYZING AGENTS

By DR. ANDRÉ KLING

*Director of Municipal Laboratory of Paris*

AND M. DANIEL FLORENTIN

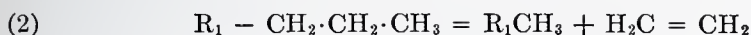
*Subdirector*

*Read by James Aston, Professor of Mining and Metallurgy, Carnegie Institute of Technology*

Until recently the syntheses of organic chemistry, which were so brilliant, were made not very much above ordinary temperatures.

Since the velocities of reactions are considerably greater at high temperatures, it seemed interesting, in the view of extending the possibilities of results, to increase the temperatures of the reaction. Unfortunately, however, there was an obstacle to the proposed attempts in the fact that organic molecules are unstable, especially when molecular weights are high. The limits of temperature above which most of the somewhat complicated organic molecules cease to be stable are relatively low. For each organic molecule there exists a beginning point of decomposition above which dissociation occurs the velocity of which increases with the temperature. In addition, though organic molecules do not differ from inorganic ones, dissociation of a mineral molecule  $AX$  above its temperature zone of stability follows the well known laws of thermo chemistry:<sup>1</sup>  $AX \rightleftharpoons A + X$ , the velocity of dissociation increasing with the temperature, without any modification, generally, in the type of reaction, while organic molecules, owing to the complexity of possible reaction, may furnish different types of dissociation. If we consider, for instance, a very simple type of organic molecule, like  $C^n H^m$ , we observe, at the beginning of decomposition, several types of molecules in the products.

If we take, for instance, the dissociation of saturated aliphatic hydrocarbons at  $470^\circ C.$ , the most probable equation of dissociation or, more exactly, the most predominant one may be written:



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<sup>1</sup> H. Gault, *passim*.

At higher temperatures the attraction between atoms of carbon and hydrogen becomes less; free hydrogen appears and, at the same time, unsaturated hydrocarbons are formed, which, being unstable are polymerized immediately after formation. The molecules form the most stable type, that is the cyclic one. Naphthenes and, at least, aromatic hydrocarbon appear. When the temperature increases the hydrogen content in the gas increases and hydrocarbons, always richer in carbon, are observed leading at the end to cracking cokes.

This process of obtaining light saturated hydrocarbides starting from heavy ones, sacrifices an important part of the primary products by partial retrogression towards a molecular form close to certain allotropic varieties of carbon.

Since at temperatures of 500° or above, each type of reaction occurs with its proper velocity, it is possible to foresee how complicated will be the results. In addition, reactions may not be reversible, as reaction,<sup>2</sup> not only because at a given temperature several reactions occur simultaneously, but also because formed products are modified almost instantaneously either by polymerization, or by new dissociation.

It does not seem that the investigators, who studied dissociation and cracking, have given a sufficient attention to considerations relating to the particular state of molecules. In fact organic molecules during thermic dissociation are in a particular state, "the nascent state," as we intend to show.

All chemists know that, to react, molecules must be in a particular state, so as to have intimate contacts. The old sentence "*Corpora non agunt nisi soluta*" has in view a particular case, where ionization of molecules occurs owing to the action of a solvent, generally water. The gaseous state, by its particular physical condition, is also favorable to chemical reactions. Many gases, however, have been until recently considered inert towards certain other gases, for example, hydrogen towards nitrogen or towards most of the organic molecules and particularly, hydrocarbons. But chemistry has been enriched by the new method of using catalyzing agents, and it has been made possible to increase the reactivity of many substances, chiefly gases, thereby extending considerably the field of chemistry.

Considering only the particular case of hydrogenation, let us remember that hydrogen, evolving in certain reactions, possesses in

<sup>2</sup> H. Gault, *passim*.

the nascent state a special reactivity, so that special reductions or hydrogenations take place; we may quote, for instance, the reduction of silver chloride by nascent hydrogen, evolved when zinc reacts on sulphuric acid, and particularly all those remarkable hydrogenations obtained by Berthelot with nascent hydrogen produced by thermal decomposition of hydriodic acid. By this process, called by him "universal system of hydrogenation" this master could hydrogenate a large number of organic substances, including coal, which he converted into liquid hydrocarbons.<sup>3</sup>

On the other hand molecular hydrogen has been considered for a long time as an inert gas. By the use of catalyzing agents, however, and more particularly by the so called hydrogenating catalyzing substances (nickel, iron, cobalt) it has been made possible to fix directly molecular hydrogen at normal or at high pressure on many organic molecules. It seems that, in such cases, the catalyzing agent atomizes molecular hydrogen, that is, splits the molecules into atoms, owing to the formation of unstable intermediates and by this process the pressure of the gas within the pores of the reduced metal is considerably increased. We shall prove, at least in several cases, that pressure alone is not sufficient to allow fixation of molecular hydrogen on the atoms of carbon of a stable organic compound, when such fixation is made possible by the use of an hydrogenating catalyzing agent.

We must, in addition, consider that another process here determines a special and spontaneous reactivity. That is the cracking process. Cracking of hydrocarbons leads to light products, like hydrogen, methane, ethylen, the lower aliphatic hydrocarbons together with liquids (olefines, petrols) and also to highly condensed substances like tars and even cokes. Cracking tars, like all carbonization tars, result from the condensation of many atoms of carbon of the acyclic as well as of the cyclic series. Such a condensation occurs when heavy molecules are dissociated, because, at that time, a number of the bonds of carbon atoms are freed by evolution of atoms of hydrogen or of light hydrocarbons ( $\text{CH}_4$ ,  $\text{CH}_2 = \text{CH}_2$ , etc. . . .) and must be united together so as to produce a stable compound, as it is impossible that those bonds remain free, the molecules to which they belong being unsaturated. When they appear, these incomplete molecules possess a special reactivity, which has been used in certain methods of hydrogenation at high pressure and high temperature.

<sup>3</sup> Bull. Soc. Chim. Paris, lx (1868), pp. 8 and seq.

For many years catalyzing agents have been used in cracking processes. Ritmann, MacAfee, and many others have used aluminium chloride, which had been made known by the works of Friede and Craft (1880), as an agent which would cause rupture of organic molecules and further regrouping. Professor Franz Fischer has used this substance (1916) to transform naphthalene into liquid hydrocarbons at normal temperature; he obtained hydronaphthalenes together with a small quantity of benzenic hydrocarbon.<sup>4</sup>

It seems that the action of aluminium chloride may be explained by intermediate formation of compounds, the zone of thermal dissociation of which should be below the decomposition zone of primary products. Our personal investigations have proved that such a mechanism is not mere hypothesis.

Dr. Bergius has taken advantage of that thermal dissociation of organic molecules and of the very special reactivity of fragments of molecules resulting from that dissociation in his direct method of hydrogenation of organic molecules at high temperature and high pressure. In his process, heavy hydrocarbons are heated at 400° to 450° in presence of hydrogen. Dr. Bergius has given the following definition of his process: "a process to decompose carbon compounds having a high boiling point, into gasoline with transformation of unsaturated compounds into saturated ones, by means of heat in presence of compressed hydrogen and under a pressure of at least 20 atmospheres, the process being characterized by the fact that it is worked out without any catalyzing agent."

Hence in the Bergius process no use is made of any catalyzing agent and Dr. Bergius has insisted several times upon this new feature of his direct hydrogenation method, taking care to prove that the steel wall of his retort had no appreciable effect in the reaction.

We do not think we betray Dr. Bergius when admitting that, by catalyzing agents, he had in mind hydrogenating agents of the nickel group, the use of which had been published by several authors, following the work of Sabatier and Senderens and of Ipatief, who used, as is known, hydrogen under pressure.

When we began in 1923 to study this process of hydrogenation, we verified the correctness of the theories of Dr. Bergius, as we could observe a fixation of hydrogen together with formation, at least for acyclic compounds, of light saturated products.

But when we tried to extend to other series such experiments, we

<sup>4</sup> D. R. P. 299.134, D. Ber. G., xlix (1916), pp. 252.

found that certain products could not be hydrogenated or at least that there was some difficulty in obtaining a fixation of hydrogen. Bergius' process appeared then not to be of general use, as had previously been supposed.

When, for instance, light hydrocarbons such as pentane and hexane could be easily obtained from heavy petrol residuals, paraffines, etc. On the other hand naphthalene, anthracene, phenol ( $C_6H_5OH$ ), when treated, remained almost entirely unaffected, even when the temperature had been raised to  $500^\circ$  and the pressure to  $250^\circ$  kgm. per square centimeter (3750 pounds per square inch).

We started then to study systematically several products and concluded that, generally speaking, if hydrogenation was wanted, it was necessary to obtain a rupture of actual molecules or, at least, rupture of certain functional groupings. We realized that hydrogenation resulted from fixation of molecular hydrogen on molecules actually submitted to thermal dissociation, that is in a nascent state and that as soon as the unsaturated molecule became stabilized in its normal molecular state it was nearly impossible to obtain hydrogenation.

It was then very important to determine for each group of substances the point at which the dissociation began under operating conditions—that is under pressure of hydrogen.

We found the following figures:

	<i>degrees C.</i>
Tertiary butyl alcohol.....	250
Secondary butyl alcohol.....	380
Paraffinic hydrocarbons from.....	410-440
Vegetable oils.....	410
Naphthalene.....	475
Anthracene.....	440
Resin (colophany).....	460

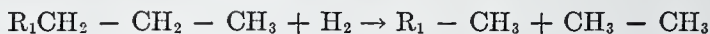
The fixation of hydrogen is obtained under pressure, becoming sensible for pressures above 100 kgm. per square centimeter (1400 pounds per square inch) and increases with pressure. Dissociation of heavy molecules depends upon the temperature; as soon as the dissociation point has been reached, the velocity of dissociation increases rapidly with temperature increase.

If we desire to obtain an effective hydrogenation with formation of saturated compounds, it is then indispensable for a given pressure of hydrogen, to increase the temperature moderately, and to reach a

point where a balance can be sensibly obtained between velocity of dissociation and velocity of hydrogenation of nascent molecules. If we exceed that optimum temperature, pressure increases instead of decreases as would be the result from the fixation of hydrogen. Cracking occurs and not hydrogenation; liquid and gases produced are rich in unsaturated compounds. A too vigorous cracking action would even lead to formation of tars and also of coke, when normally dough-like products become fluid.

When hydrogenation occurs at about the beginning of dissociation the reactions are very simple and the gases contain less methane.

If we take into consideration studies made by Norton and Andrews, Haber, H. Gault, etc., we may write as follows the first phase of the reaction for paraffine hydrocarbons:



If hydrogen had not been present, we should have obtained ethylene  $CH_2 = CH_2 \cdot R_1CH_3$ , having a stability not very different from the stability of primary product ( $R_1C_3H_7$ ), is also dissociated and so on.

The farther we go the more we obtain gases and light hydrocarbons, diminishing the proportion of untransformed hydrocarbons. Practically, in a closed vessel, the initial product is not integrally transformed into a light one so that we obtain the complete series of all possible hydrocarbons from methane to primary products.

Practically the dissociation zones of acyclic compounds are sensibly below those of cyclic compounds and chiefly of aromatic compounds.

From the above, we may conclude that if we start from a raw material made up of acyclic and cyclic constituents and if we undertake hydrogenation at a temperature of a few degrees above the beginning of the dissociation of acyclic compounds, we shall obtain light products derived from acyclic constituents, while the cyclic components will remain practically unaltered. We shall observe that acyclic products lead always by hydrogenation to aliphatic hydrocarbons and that cyclic and aromatic series lead to derivatives having also a cyclic constitution and containing but a small proportion of aliphatic compounds due to the rupture of lateral chains.

Having made these preliminary observations we then studied systematically the most important fuels.

We found that a certain proportion of coals, varying according to their nature, leads by hydrogenation, to aliphatic or polymethylenic compounds. That fraction seems to correspond to the resinous

constituents (gums, resins, waxes). On the other hand, another fraction, by far the most important because of the lignin, is very stable and very difficult (even impossible without catalyzing agents) to transform into light hydrocarbons. This concurs with Prof. Franz Fischer's theories on the ligneous origin of coals.

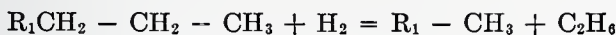
It is very curious to notice that until now we have given similar names to various fuels which are quite different in their constitutions and properties. "Bog head" of Autun (France), for instance, takes its origin, like shales from the same field, from spores and resins of vegetals of the carboniferous period; it easily gives light aliphatic hydrocarbons; on the other hand a Bohemian "Bog head" has a quite different structure, is very similar to the structure of the Cannel Coal of Béthune, and yields almost entirely aromatic derivatives.

Brown Coals (lignites) of the Rhine district as well as of Bohemia are generally very rich in acyclic resinous compounds. Ease of hydrogenation is somewhat connected with the tar and light oils output by low temperature carbonization.

We must at least say that hydrogenation may, according to our opinion, facilitate a study of the stability of organic substances at high temperatures and of their pyrogenous dissociation. As afore-said, when we treat pure compounds at temperatures slightly above the dissociation point, we may obtain gaseous and liquid products, the analysis of which will determine which groups of the molecule are freed. This method, if properly followed, has the great advantage of avoiding the secondary reactions of polymerization, which sometimes become the most important.

The energy involved by rupture of molecules and subsequent hydrogenation of partial fragments seems to be very low. Theoretically the phenomenon is somewhat complex. From the work of Fajans, Weinberg, Wibaut, we know approximately the energy of the union between carbon and hydrogen atoms in acyclic normal chains and in several other series.

If we consider one of the simplest cases, the one above mentioned for instance:



we see that we have a dissociation of a molecule of hydrogen  $H_2$  into 2 atoms of hydrogen; that means an absorption of 81 calories, the rupture of one bond  $C-C$  in the primary product, absorbs

70 calories<sup>5</sup> and finally the fixation of two atoms of H on two atoms of carbon, equivalent to a production of  $2 \times 80$  calories.

The final balance will then be:

$$-81 - 70 + 2 \times 80 = +9 \text{ calories}$$

Hydrogenation then means a very slight production of caloric energy.

Though we were not able with our apparatus to make very accurate measurements, it seems that hydrogenation is really slightly exothermic.

But it is clear that in industrial practice, reactions will be very complicated owing to the complication of the material treated itself, which never belongs to the normal aliphatic series.

We have noted that hydrogenation by Bergius' method was unsuccessful for compounds stable at high temperatures like polyaromatic hydrocarbons, phenols, and all substances with which pyrogenous dissociation occurs at very high temperatures (not practicable with apparatus generally used).

It appeared to us at once that we should be able to make hydrogenation easier by using a catalytic agent capable either of forming intermediate products having a lower grade of stability than primary material, or of creating a rupture of the molecule by the removal of functional groups.

Experience has completely confirmed our theory and we shall examine in this paper the two main categories of catalyzing agents used by us with actual success.

#### CATALYZING SUBSTANCES WITH ADDITIVE ACTION BY SUBSTITUTION OR DEPOLYMERIZATION

We shall first describe the general conditions of operation in laboratory tests: 250 to 300 grams of material to be tested were heated in a rotating steel bomb of 2 liters capacity under an initial pressure of hydrogen of 70 to 100 kgm. per square centimeter (1000 to 1400 pounds per square inch) corresponding to working pressures of 200 to 300 kgm. per square centimeter (2800 to 4200 pounds per square inch), with or without appropriate catalyzing substances. Curves of temperatures and of pressure were simultaneously recorded, the curve of pressure serving as a guide in following the reaction.

<sup>5</sup> Corresponding to a vaporization heat of diamond equal to 150 calories.

Gaseous and liquid products evolving during a test were totally and carefully collected and submitted to analysis. This analysis gives an explanation as to which reactions occurred.

We have said that polynuclear products of aromatic series, such as naphthalene, anthracene, and phenanthrene were dissociated only at high temperatures, and that consequently, transformation into light hydrocarbides even in presence of hydrogen at high pressure was not satisfactory. In fact, such hydrocarbides may be slightly hydrogenated without a catalyzing agent, when atoms of hydrogen are fixed on the double bonds of the benzene nucleus in the molecules of such hydrocarbons. We may then observe, before thermal dissociations occurs, a loosening of aromatic double bonds sufficient to permit direct fixation of hydrogen with production of hydroaromatic hydrocarbons. At high temperatures the rupture of certain molecules occurs simultaneously and a small quantity of mononuclear aromatic hydrocarbons like benzene, toluene, etc., is formed.

But as hydrogenation was so difficult we thought that by helping the action of hydrogen by the action of a catalytic agent able to create an intermediate addition or substitution product, we could obtain a noticeable reduction of temperature for initiating dissociation. This at once suggested the use of halogen compounds of the aluminum and iron groups and also halogen compounds (such as antimony chloride) having the property of accelerating substitution.

For naphthalene, aluminium chloride very sensibly lowers the initiation of dissociation below  $460^{\circ}$ , and the production of oils increases from 30 to 60 per cent at  $460^{\circ}$ ; in addition *oils* contain more mononuclear benzenic compounds: 55.6 per cent instead of 25 per cent. Hence the catalytic agent not only reduces the temperature of the initiation of decomposition but also creates a rupture of the molecule and permits the production of benzoles distilling on an average between  $80^{\circ}$  and  $160^{\circ}$  (for 60 per cent of produced oil).

Similar results have been observed with anthracene and other hydrocarbons of this series. With anthracene for instance, the initial temperature of dissociation is about  $440^{\circ}$  and has been reduced to  $425^{\circ}$  to  $430^{\circ}$ ; the proportion of liquid products has been increased and in the liquid fraction a noticeable proportion of benzole distilling below 160 is found (36 per cent), the other liquid products being hydrothracenes.

It is very important to add but a small quantity (1 to 5 per cent maximum) of the catalytic agent; otherwise rupture and polymeriza-

tion would prevail instead of hydrogenation; and in such a case we should obtain a product containing large quantities of solid substances insoluble in benzene.

The anthracene nucleus is particularly fragile with regard to this character and ferric chloride gives better results than aluminium chloride.

Another series of substances that may be treated with such catalyzing agents are the highly condensed products like tars, pitches, etc., and also compounds with contiguous nuclei like resin, lignine and derivatives.

Theoretically, as aforesaid, we may regenerate tars resulting from a polymerization of incomplete molecules evolving during a violent pyrogenation of organic compounds by action of heat in presence of hydrogen under pressure. Practically, however, for highly condensed tars, like coal tar pitch, this process is troublesome as hydrogenation proceeds very slowly.

Activation is obtained by addition of catalyzing agents, like aluminium chloride, which act as depolymerizing substances, as explained above.

We made experiments with petroleum tars and pitches as well as with coal tars and pitches. From the first group we obtained gasoline and petroleum of the acyclic type; from the second we could obtain benzenic compounds. We can conclude from those experiments that tars of various classes keep the structure of the molecules, from which they were derived.

#### CATALYZING AGENTS WITH DEHYDRATING ACTION

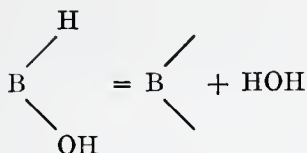
There exists a category of substances which resist the action of heat, hence that of hydrogenation. They are the aromatic phenols.

Phenol ( $\text{C}_6\text{H}_5\text{OH}$ ) more particularly may be heated to  $500^\circ$  without being appreciably transformed.

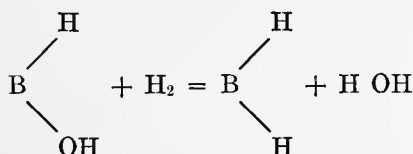
It was then very important to remove the functional hydroxyl group and we have had in mind utilization of dehydrating catalyzing agents, which would eliminate hydroxyl by transformation into a molecule of water.

Many works about this subject have been published;<sup>6</sup> we always obtained unsaturated hydrocarbons, as a double bond forms in the schematic reaction.

<sup>6</sup> Bull. Soc. Chim. France, xli (1927), pp. 1341.



If, on the other hand, we heat a phenol in presence of hydrogen under high pressure and also of a dehydrating catalyzing agent, even in the liquid phase, we obtain the corresponding saturated hydrocarbon



Dehydrating catalyzing agents are numerous as has been proved by Sabatier and his disciples.<sup>7</sup> We may quote alumina, aluminium phosphate, clay, silica, thoria, vanadium oxide, chromium oxide, titanium oxide, zinc oxide, zinc chloride, tungsten oxide, molybdenum oxide, etc. Preference is given to a particular one according to economic conditions and special activity.

The activity depends largely upon means of preparation and grade of polymerization resulting from it.

By way of proving the mechanism of hydrogenation we treated ordinary phenol ( $\text{C}_6\text{H}_5\text{OH}$ ) without a catalyzing agent, under an initial pressure of hydrogen of 90 kgm. per square centimeter (1250 pounds per square inch). After two and one half hours even at temperatures of  $460^\circ$  to  $470^\circ\text{C}$ ., the phenol remained unattacked. In presence of alumina, 45 per cent of phenol was transformed into benzene hydrocarbons after four hours. If we repeat that experiment, but substitute for hydrogen an inert gas like nitrogen, at a similar pressure (80 kgm. per square centimeter or 1120 pounds per square inch) we obtain after four hours a black viscous liquid containing 5 per cent only of low *boiling* hydrocarbons, and 15 per cent of a tarry residual at  $270^\circ$ .

These experiments prove:

1. That without a catalyzing agent phenol is not attacked even in presence of hydrogen.

<sup>7</sup> Sabatier, *Catalysis in Organic Chemistry* (1913), pp. 178 and seq.

2. That in presence of a dehydrating catalyzing agent phenol is dehydrated to a certain extent, but incomplete molecules resulting from that dehydration are linked together so as to produce condensed products or tars.
3. That in presence of a dehydrating catalyzing agent and of hydrogen under pressure, phenol is transformed quite easily into benzene hydrocarbons.

Cresoles are transformed likewise, the efficiency being somewhat greater than the phenol.

Naphthol treated during four hours at  $470^{\circ}$  to  $480^{\circ}$  by hydrogen at high pressure in presence of a dehydrating catalyzing agent is transformed partially (33 per cent) into a liquid mixture of benzene hydrocarbons and hydronaphthalene. The solid residual is almost exclusively naphthalene and solid hydronaphthalenes. To sum up, naphthol is transformed into naphthalene and partially into hydronaphthalene and benzene hydrocarbons, resulting from the opening of one of the two nuclei of naphthalene.

Cyclohexanol and other cyclanols are by this process transformed very easily into light hydrocarbons of the aliphatic hexanic series which result from the opening of the cyclic chain.

Identical results are of course obtained when treating industrial products of similar nature, like phenolic oils, low temperature tars (either coal or lignite).

Natural products are generally complicated as they contain constituents of dissimilar structure and possess chemical functions. That is the case for coal or lignite tars (either high temperature or low temperature tars) which contain besides mononuclear aromatic hydrocarbons, polynuclear aromatic hydrocarbons, aromatic phenols and very often hydrophenols.

Most of the substances used as fuel are constituted, as aforesaid, of resinic compounds, derived from resins, gums and waxes, associated with other compounds belonging to the aromatic series derived from lignin and possessing a certain number of hydroxyl groups free or substituted.

Our researches led to the conclusion that hydrogenation of complicated substances had to be done in presence of appropriate mixtures of catalyzing agents and by successive treatments at various given temperatures, each temperature corresponding to a given catalyzing agent. Those agents belong to the two categories we have just described. A few are mixed, that is possess different actions.

Such agents, like the ones which possess a hydrogenating action (oxides of polyvalent metals, for instance) are very useful in certain cases.

Our researches were first made on a laboratory scale, but they have now been transferred to an industrial stage. Very promising results have been obtained.

A low temperature coal tar, for instance, having been dehydrated and freed from light oils distilling below 205° has been hydrogenated; a very fluid liquid with a density of 0.910 has been obtained.

Fractions of this liquid gave following results:

FRACTION	DENOMINATION	PERCENTAGE	$D_{18}$
<i>degrees</i>			
55-120	Light spirit	15	0.720
120-180	Middle spirit	26	0.821
180-205	Heavy spirit	10	0.924
205-230	Petrol	23	0.969

The two first fractions did not contain any phenols, the third contained but 20 per cent and after dephenolizing treatment density was reduced to 0.885.

In addition 6 to 8 per cent of gasoline was removed by means of activated charcoal from gases evolving during hydrogenation.

Lignite tars from brown coals gave similar results; a very suitable motor fuel was obtained as it contained a mixture of aromatic and aliphatic hydrocarbons.

The phenolic oils of coke oven tars gave 10 per cent of gases and 90 per cent of a liquid with a density at 18 of 0.950. By fractionation this liquid gave:

FRACTION	PERCENTAGE	$D_{18}$
<i>degrees</i>		
70-120	23	0.876
120-180	40.6	0.910
180-210	21	

The second fraction still contained a small quantity of phenols After a soda washing the density was reduced to 0.890.

Phenolic oils may then be treated to give benzoles (benzene, toluene).

Various solid fuels, adequately chosen according to the principles given in this paper, when treated alone, or better when treated in presence of a certain quantity of heavy oils, give either aliphatic hydrocarbons or mixtures of aromatic and aliphatic hydrocarbons.

We then believe that our views open a very broad field of researches, interesting on the side of theoretical chemistry as well as applied chemistry and particularly motor fuel chemistry.

We learned recently from a paper printed in "Stahl und Eisen" of July 7, 1927, that the "Interessen Gemeinschaft für Farbenindustrie" ceased to apply the direct hydrogenation method of Dr. Bergius and that, proceeding from theoretical views quite similar to ours, used catalyzing agents; but we believe that we are the forerunners in this field as our work was done in 1924 and 1925 and partially disclosed in the early days of 1926.

#### DISCUSSION

DR. ELWOOD B. SPEAR (Thermatomic Carbon Company, Pittsburgh, Pa.): I should like to put this one question: Is it the experience of the gentlemen who have carried out this work that there is a deposition of carbon on the catalytic agent at the high temperatures?

DR. BING: We did find it under certain temperatures which are not practical for catalysis. We found a change in the crystallization chiefly, and an alteration by cyanide compounds and also by sulphur. But, a carbon deposit can be found at high temperatures.

DR. SPEAR: May I also suggest that the results as given in terms of the volume of the catalytic agent are not very illuminating sometimes. Is it possible to give the results in some measure of the surface exposed on the catalytic agent and of the total volume?

I gather from the paper itself that the surface is undoubtedly changing. It is crystallizing and therefore the total amount of surface exposed will be changing.

The purpose of my question is: "Does it make any particular difference what that surface is, or is it a question of the total amount of surface exposed to the reaction?"

DR. BING: The measurements have been taken when the catalyzing substance was acting. As soon as the crystallization changes it drops quickly and there is no more question of surface or yield. The yield was constant as long as we had the several experiments which cost about \$300 or \$400. The change of yield was inconsequential. As soon as it drops so quickly then the surface is changed.

DR. A. E. DUNSTAN (Institution of Petroleum Technologists, London): I would like to ask Dr. Bing concerning just one point. There is a parasitic reaction (illustrating on the board—indicating Equation No. 4, page 518). Some years ago we had a problem in our field in Persia, of disposing of great quantities of methane. At that time we were very much attracted by the possibility of reversing this reaction (Equation No. 4, page 518).

DR. BING: We are studying that problem.

DR. DUNSTAN: We did heat methane with steam up to about 2000 or 3000 pounds pressure at varied temperatures. We skipped this reaction (Equation No. 4) and went straight here (Equation No. 1, page 518). We obtained the starting out material that you were discussing this morning.

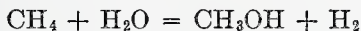
Have you come across any method of reversing this (Equation No. 4)?

DR. BING: We are now making experiments along that line. The first experiments we have done have been somewhat difficult because we are using catalyzers containing certain substances. I believe these will be disclosed in one year or more. We are just starting these and we found many difficulties in the problem because the two reactions are difficult to separate.

DR. DUNSTAN: If there is any one in the petroleum industry who is faced with a vast amount of gas they want to use the reaction that is here (Equation No. 4).

DR. BING: We had partial success, but we did not master the reaction.

DR. P. K. FROLICH (Massachusetts Institute of Technology, Cambridge, Mass.): Regarding the formation of methanol from methane and water as mentioned by Dr. Dunstan, the equilibrium constant is, if I remember, about  $10^{-16}$ . Assuming that a temperature of about  $500^{\circ}\text{C}$ . would be required for activating the methane, there would hardly be any methanol in the equilibrium. Furthermore, since the reaction goes without change in volume, pressure will have little or no effect. It therefore seems a hopeless task to prepare methanol by the reaction.



I was particularly interested in one point of M. Audibert's paper, namely, the x-ray examination of the metallic oxide catalysts. If I understood Dr. Bing, the freshly prepared catalysts did not show any marked diffraction lines, thus indicating the absence of large crystals in the mass. However, after exposure to higher temperature during use in the methanol reactor, crystals gradually developed. While this result would be expected in the case of pure single component catalysts, such as zinc oxide, copper oxide, or metallic copper, I would be very much interested in knowing whether Audibert has made similar experiments with *mixed* catalysts. In light of Wykoff's studies of ammonia catalysts, from which he concluded that the sole function

of aluminum oxide was to prevent the crystallization of the iron forming the base of the contact substance, one would naturally expect that mixtures of metallic oxides would have considerably less tendency to recrystallization. Has any work of that kind been done?

DR. BING: We are now trying what will happen if we mix a catalyst within 400 hours, to see whether the catalytic agent ceases to be active. We are trying to find a method of analysis. We have had the spectrum and now we must wait a long time because we have noted the changes in the catalytic substances. That is the object, to see what happens after 300 or 400 hours. It takes a very long time to get a substance ready for examination. It takes about three weeks for two experiments. We have no definite conclusions now. We know there is a change, but we do not know how that is, or what will change the catalysts. It takes a long time to study that. It is something that we are starting and it may last for five or six years.

DR. FROLICH: But what do you expect to find by x-ray examination of mixed catalysts?

DR. BING: We will find something and we want to see what it is.

DR. FROLICH: It will at least be interesting to see if the recrystallization does not go slower with mixed oxides, since this would be in line with the longer life of such catalysts as compared with those consisting of one single component.

There is another point which has puzzled me somewhat, and that is the contradictory results obtained by different investigators who have studied the same types of catalysts for the methanol reaction. Patart in his early work used copper catalysts, but finally found that metallic oxides, like zinc and chromium oxide, etc., were superior to copper. Audibert on the other hand, finds that copper base catalysts are superior to zinc oxide.

DR. BING: Both may be used but with the zinc you may use gases which are not so pure.

DR. FROLICH: I think that your data in this paper and in a recent publication, in *Industrial and Engineering Chemistry*, actually show lower yields with zinc oxide.

DR. BING: The yield with copper is higher, but from the financial point of view it may be more expensive. It depends on the relative cost of the catalytic substance and the cost of the plan and also the cost of the purification. If you are obliged to purify to a large extent, and if it is very expensive, you may lose the advantage of the copper. We cannot tell you what will be the more practical in industry.

DR. FROLICH: I am sorry that I did not have a chance to finish my remarks since I was driving at a somewhat different point, namely, the fact that our

experiments at Massachusetts Institute of Technology confirm Patart's conclusion to the effect that the metallic oxides are superior. As a matter of fact, we have found copper to be exceedingly inactive both in the synthesis and in the decomposition of methanol.

One possible explanation for these discrepancies may be that Audibert in his experiments precipitates the copper with sodium hydroxide and therefore undoubtedly includes some alkali, which acts as a promotor. Even by the most careful washing, such as is generally practiced in analytical chemistry, one cannot remove the last traces of alkali, and we have shown in papers presented at the recent meeting of the American Chemical Society at Swampscott, that this small amount of alkali is sufficient to cause a manifold increase in the activity of the resulting copper catalysts. It is only by dialysis over a period of several weeks that an alkali precipitated copper hydroxide can be freed of these impurities, so as to show the lack of activity characteristic of ammonia precipitated catalysts.

DR. BING: We do not tally with you on that. It depends on the way you obtain the copper, but traces of alkali are not found. I think Jean Proctor, when making his experiments, prepared his copper in another way. He has a way of getting around that which has been shown in this paper. But traces of alkali are not found in our catalysts as far as I know.

That question has been asked by representatives of the government and of industry. It has been answered that there were no traces of alkali in our catalytic agent. The way the copper has been obtained is very important. I say a few words in the paper about it. It seems the physical state of the catalyst is of great importance. Also, the way you operate the initial catalyzing agent or system is important.

DR. FROLICH: Please keep in mind that I am simply trying to find an explanation of the discrepancies between the results obtained in the various laboratories. When working in this field one naturally becomes desirous of finding some sort of an explanation for the divergencies observed, and it seems to me that the promotor action of occluded alkali fully accounts for the high efficiency of copper catalysts reported by Audibert. In going through previous publications by the author, I have not found anything which contradicts this viewpoint. However, there is of course, a possibility that some special method of catalyst preparation has been employed, and that this has not been disclosed.

DR. BING: It will be disclosed. It is nothing which is a secret. We have no personal interest and no patents to sell. But, it will be disclosed and it is very important.

DR. ALEXANDER LOWY (University of Pittsburgh, Pittsburgh, Pa.): Can nickel be used to effect this chemical change?

DR. BING: Nickel is on the list of possible catalysts but the reaction given with nickel is quite different. Nickel belongs to the iron group. We made studies of that as a catalyzer and that belongs to a different class.

DR. LOWY: You get more hydrocarbons?

DR. BING: If I should speak of that it would last for another hour. I think I had better leave that for another time.

DR. J. L. SHERESHEFSKY (Mellon Institute, Pittsburgh, Pa.): Going back again to the question of surface. Being a process involving contact catalysis the surface of course plays an important rôle in the reaction. The question arises whether care was taken during the experiments to have the catalyst packed uniformly, because if it was not the amount of surface per unit volume of catalyst would vary with each case. If packing was uniform in all those cases the surface would remain approximately constant through all the experiments.

DR. BING: Packing of catalysts has been studied. We believe we had a constant surface. We are trying to see what will be the effect on that. These questions are very complicated because we cannot measure the surface of contact. It is not well defined.

The external surface did not change a great deal until we had a drop in the yield. At that time we were sure there was something wrong. There is some change in the crystallization. We stopped at a certain time in the other experiments. There no changes were observed. Whether it was a change in the internal structure nobody knows. Those things are possible in industrial experiments. You can change the packing so as to see the difference.

DR. L. GRUNWALD (Brevets Lefranc, Paris): I am a friend of Dr. Kling and I want to bring out that he has not mentioned all of the fine works that have been carried on by these two Frenchmen. I think that ought to be included.

DR. DUNSTAN: I should like to say that my own work over the last five or six years has been along similar lines to that described this morning.

We started out with the angle after taking the example of low temperature tar, we have there phenolic bodies and pseudo-phenols soluble in sodium phenolate. If one cracks that mass one obtains naturally light gasolines from the bulk of the material. But one degrades, or simplifies, the phenols, and the pseudo-phenols into phenols and creosols.

The whole point then was how to handle this simplified phenolic content. We tried a variety of hydrogenations with a variety of contact bodies, without specifically dealing with the dehydrating catalysts. We did find in that the presence of ammonium compounds and we also found that they brought about precisely similar reactions to those described.

I did not quite get in the paper the yields of products in these reactions. The reader of the paper presumably gave analyses of the butylene produced, but did not give the actual yields of the raw material. That is the point I would like to raise now.

In connection with the dehydrating side of phenolic substances prior to hydrogenation, I think there the authors have actually made definitely a new contribution to the science of hydrogenation.

DR. BING: That is not in the paper.

DR. DUNSTAN: In our own yield, cracking a low temperature tar, the yield of spirit is of the order say of 20 per cent.

DR. BING: In answer to Dr. Dunstan, another paper deals with the cracking of low temperature tars. The experiment was not made by Dr. Kling. It was made at the Paris Society by Dr. Mailhe of the Sorbonne. I think that is in complete agreement with what you have found.

We have found another very easy method to decompose the tar into two or three fractions and one is treated by a special process. That will be disclosed this afternoon.

DR. DUNSTAN: This point will also be discussed in my own paper Saturday morning.

DR. RALPH L. DODGE (Lazote, Inc., Wilmington, Del.): I would like to correct an erroneous impression that may have been left in the minds of the audience regarding the first paper by Mr. Audibert.

Dr. Frolich has said that calculations made in this country have indicated that it is impossible to accomplish the synthesis of methanol directly from methane and steam.

Dr. Dunstan has pointed out that he succeeded in England in making carbon monoxide and hydrogen from methane and steam. Mr. Audibert has just reported that in France he has accomplished the synthesis of methanol from carbon monoxide and hydrogen. Obviously it is possible to avoid the American's thermodynamic limitation by a combination of the experimental work from England and France.

## LOW TEMPERATURE TAR

By DR. A. MAILHE

*Professor at the Sorbonne, Paris*

*Read by Jean Bing*

The carbonizing of bituminous coals at temperatures below 500° produces a tar called "low temperature tar," which has very different properties from the tar obtained through the tar-manufacturing processes employed in coke ovens at gas works.

Bitumens are composed of hydrocarbons, generally of a low stage of oxidation or united with sulphur. They are the specific constituents of asphalts. They may be known from other carbonaceous compounds, such as lignite or coal, by their particular reactions with certain solvents, like carbon bisulphide, chloroform, the aliphatic and aromatic hydrocarbons, ether, ethanol, and others. These bitumens are commonly supposed to have resulted from an evaporating of liquid petroleum together with simultaneous oxidation.

The word "bitumen" has been extended to include derivatives of coal. For instance, the sticky residue of tar distillation, that is the pitch, is composed of hydrocarbons and has a striking resemblance to natural bitumens, although differing in some of its chemical properties.

Lignites are customarily considered as sub-bituminous coals. Since they sometimes contain 50 to 55 per cent of moisture, the large water content has been suggested as the specification for differentiating lignite from the lowest grade bituminous coals. The Geological Survey of the United States has, however, described coal fields in the Mississippi valley of indubitable bituminous nature, where moisture is over 10 per cent. On the other hand lignites may be found in the Minervois field, France, where moisture is less than 10 per cent (between 3 and 7 per cent), but where the percentage of ash is very high.

The treatment of lignites with benzole yields lignite wax and resin. In its chemical composition wax is similar to the beeswax manufactured from alcohols and esters of montanic and carboceric acids. The treatment of coals, on the other hand, by benzole yields products wholly different from wax and resin, for the result is a bitumen from the cyclic compounds (Pictet).

According to certain authors, such as R. V. Wheeler, bituminous ingredients of fuels seem to come from waxes and resins preëxisting in vegetals, which are only slightly modified in lignite, but which are completely metamorphosed into bitumen in coal. We must, however, acknowledge that in certain lignites, e.g., those from the Minervois fields, treatment by benzole or other solvents gives a very slight amount of wax—5 to 10 per cent. When, however, the resin content reaches 90 to 95 per cent, we ought to be able to conclude correctly that either those lignites were formed from resinous vegetals, or wax has been slowly modified so as to become bitumen. Those lignites give off a large quantity of tar, 9 to 12 per cent in weight, even though their ash content is very large.

We know, according to Fischer and Schröder, that humic acid is changed in time by pressure and temperature into humine, which eventually becomes a bitumen, belonging to bituminous lignite and coal.

After a microscopical study of lignites, sub-bituminous coals, cannel and bituminous coals, Thiessen has demonstrated that these latest coals, found in the oldest measures, are more complex than the cannel coals, and more like the lignites.

In 1913, White and Thiessen found cuticules of plants in several terms of this series of fuels,—the lignites, the sub-bituminous, and the bituminous coals.

White has proved not only how incorrect was the hypothesis, which is very current, that coals of old formation do not contain resins, but also that it is possible to find small parts of resin in the coals of the oldest measures.

We may then safely consider the lignites, rich in resins and bitumens, as members of the group of bituminous coals. This consideration, however, should not preclude the fact that the action of certain solvents on the various members of the series does not necessarily yield products with the same properties.

We shall find it interesting, then, to study first the low temperature tar obtained from those bituminous lignites, found in the Minervois area, composed of 40,000 acres with important centers at Bize, La Caunette, and Agel. Those lignites, distilled at a low temperature, give as does bituminous coal, very large quantities of phenols. The proportionately large amount of oxidized compounds is a distinguishing characteristic of the primary tars of most coals.

## I. DISTILLATION OF LIGNITES AT A LOW TEMPERATURE

We have distilled in an iron tube, surrounded by a lead bath, many samples of lignites from La Caunette and Bize, at temperatures below 500°. In order to facilitate the removal of products and the prevention of cracking, we provided that a small quantity of super-heated steam should flow simultaneously into the tube.

This operating process, recommended by us for ten years, makes possible the heating of lignites and also of coals, so as to obtain a low temperature tar with uniformly good quality—all done easily.

We started with a sample containing 17 per cent of ash and 4 per cent of moisture. It weighed 200 grams in pulverized form. We heated it progressively—steam flowed through the tube. We condensed the tar and steam at the outlet and collected gas. Our results were as indicated below:

1. Between 200° and 250° a small quantity of tar and a few bubbles of gas appeared.

2. At 310° gaseous production became more regular. One liter of gas being collected together with 5 grams of tar.

3. At a temperature between 345° and 350°, we collected 8 grams of tar—the volume of gases amounting to  $2\frac{1}{2}$  liters, the composition of which was as follows:

	<i>per cent</i>
H <sub>2</sub> S + CO <sub>2</sub> .....	24.5
CO.....	6
CH <sub>4</sub> .....	7.5
H <sub>2</sub> .....	60

4. At a temperature between 380° and 385°, we collected 10 grams of tar and 3 liters of gas, the latter being composed as follows:

	<i>per cent</i>
H <sub>2</sub> S + CO <sub>2</sub> .....	18
CO.....	14
C <sub>n</sub> H <sub>2n</sub> .....	2
CH <sub>4</sub> .....	33
H <sub>2</sub> .....	33

5. At 430° we obtained 7 grams of tar and 3 liters of gas which burned with a luminous flame, and which was composed as follows:

	<i>per cent</i>
CO <sub>2</sub> + H <sub>2</sub> S.....	21
CO.....	12
C <sub>n</sub> H <sub>2n</sub> .....	6
C <sub>n</sub> H <sub>2n+2</sub> .....	7.5
CH <sub>4</sub> .....	27
H <sub>2</sub> .....	27

6. At 460° we found 4 grams of tar and a larger quantity of gas. The ratio of ethyl and methane hydrocarbons had increased.

7. Above 460° and until 500° were reached we obtained 1.3 grams of tar and an increased quantity of tar.

Distillation of the bituminous lignite from La Caunette produced 35.3 grams of tar (17.6 per cent), the distribution of which according to the temperature of production was as follows:

	<i>per cent</i>
290 degrees.....	2.5
345 to 350 degrees.....	4
380 to 385 degrees.....	5
430 degrees.....	3.5
460 degrees.....	2
480 degrees.....	0.65

Quantity of Tar

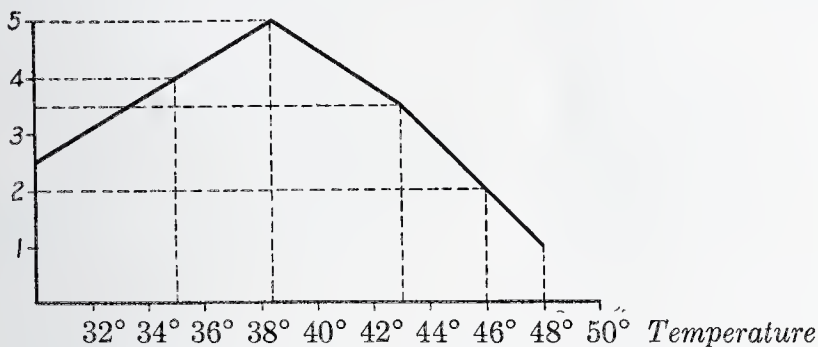


FIG. 1

Most of the tar, as the above graph indicates, distills between 345° and 460°, with the maximum production at about 380°. The distilling, for all practical purposes, may be discontinued at 460°.

Several subsequent distillations, conducted in accordance with the foregoing specifications, yielded results approximately identical with the preceding one. We then had available certain amounts of the various tars produced at the different temperatures.

The melting points of these tars ranged between 22° and 23°.

By distillation, fractionating may be obtained as shown in Table I.

From these results we may conclude that tars obtained at various temperatures do not have a homogeneous composition.

The fraction collected at 290° contains the maximum ratio of light products, 35 per cent distilling below 300°; the fraction at 345°—31 per cent; the last three fractions—nearly the same percentage of light products.

Pitch appears in small quantities in the first two fractions, but becomes important in the last three.

Subsequently, by using methanol, which is a solvent for light and middle oils as well as for phenols and resinous compounds, I treated the crude tar in order to separate paraffine and oils. When I used this process, I thought it quite new, but later discovered that it had been used in Germany by R. Seidenschnur (Cf. German Patent No. 369,883, June 27, 1919) for the removal of paraffine in lignite oils.

By employing the foregoing process in the treatment of 200 grams of low temperature lignite tar, we separated 90 grams of paraffinous residue, from which we extracted a white paraffine with a melting point of  $56^{\circ}$ , and 110 grams of soluble oils. By a soda treatment we obtained 18 to 20 grams of phenolic compounds—cresol, xylanol, and higher phenols. There remained about 80 grams of hydrocarbon oils which gave by distillation the following:

At normal pressure:	<i>grams</i>
From $170^{\circ}$ to $250^{\circ}$ .....	12
From $250^{\circ}$ to $280^{\circ}$ .....	8
At a pressure of 40 mm. of mercury:	
From $200^{\circ}$ to $250^{\circ}$ .....	18
From $250^{\circ}$ to $300^{\circ}$ .....	14
From $300^{\circ}$ to $356^{\circ}$ .....	20
Residual pitch.....	26

The last fractions have unusual viscosity, and after purification may be used as lubricating oils.

The fraction distilling between  $300^{\circ}$  and  $350^{\circ}$  (under 40 mm. of mercury) is quite solid. It contains a certain amount of paraffine, which had remained in the oil fraction after treatment by methanol. All these oils become successively brown when exposed to the air. They also are very odoriferous. It is necessary to subject these oils to careful cleaning and purification.

The carbonizing of La Caunette lignite made at a low temperature—below  $500^{\circ}$ , produces an important amount of sulphuretted compounds, which are mixed with tar and which give to all distilled fractions an unpleasant odor. The nature of the compounds is not well known. If thiophenic compounds are found, as well as mercaptans and alcoholic sulphides, it seems that certain fractions contain sulphides which possess great stability with different reagents.

We endeavored to eliminate the compounds.

The various processes which have been until now, recommended

for treating hydrocarbon oils, did not produce satisfactory results. Treatment of the light oils with soda washes, alternated with air exposure and the simultaneous action of chlorhydric acid and air, followed by soda or water-washing (Westfield process); or treatment with hypochlorite of soda washing, followed by filtration through bauxite, silicagel, or Florida earth (Dunstan process—British) has been found insufficient. Furthermore the heating of hydrocarbons with oxides of lead, iron, copper-processes which have been very often indicated, have given us unsatisfactory results with the tested products. Also if aluminum chloride should react on sulphuretted compounds, it has the disadvantage of polymerizing partially at least, lignite oils. Moreover, hydrogenation by nickel failed to remove completely the characteristic odor.

TABLE I

FLECTIONATION	TAR COLLECTED AT				
	290°	350°	380°	430°	480°
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
170° to 300°.....	35	31	26.5	28.5	25
300° to 350°.....	30	28	28	16.5	25
350° to 360°.....	25	28	6	19	16.5
Pitch.....	10	12	39	35	33

Fischer's process has not been tried. A sensible improvement, however, has been made, for odor as well as for coloration, by heating with finely powdered metals, such as impalpable nickel or copper. Several reducing agents reacting on sulphuretted compounds of lignite oils, partially destroy them.

Light lignite oils, boiling between 70° and 205°, are lightly colored when distilled. The color improves after an interval of time. The odor remains nauseous—the boiling of such oils, however, with 10 per cent stannous chloride (by weight) produces, at first, the violent escape of hydrogen sulphide and mercaptans. The stannous salt is partially transformed into sulphide. After a few hours, the quantity of hydrogen sulphide escaping is rather small. If additional stannous chloride be used, hydrogen sulphide again escapes; and after a certain period, more time is required to blacken acetate of lead paper. After this treatment, further reduction of the organic sulphides remaining in the oils is obtained with difficulty.

After cooling, the liquid is decanted, and washed with water and diluted soda. By distillation, we obtain a water-white liquid, which does not become brown to the air and possesses a pleasing odor—wholly different from the objectionable one of the primary product.

The sulphur contents are as follows:

	<i>per cent</i>
Primitive oils.....	4.3
Transformed oils.....	3.5

By treatment 1 per cent of the sulphur was removed. That quantity was probably present in the shape of mercaptans, sulphides, and thiophenic compounds. Other sulphuretted compounds, apparently, were unaltered—in spite of the fact that the light oils became odorless and colorless.

The results are more satisfactory for low temperature phenols. These compounds possess a very disagreeable odor and a ruby-red color, the latter being in time quite accentuated. These phenols are then useless for the chemical industry.

By treating, however, with stannous chloride, phenols, and conducting the distillation below 240°, we obtained products which were colorless and odorless, and which had their sulphur content reduced from 3.4 to 0.5 or 0.6 per cent. We were successful in obtaining the three cresols: ortho, meta, and para, as well as the metaxyleneol. All of these products may be used in the chemical industry.

Although low temperature carbonizing of bituminous lignites of the Minervois field gives sufficient quantities of a tar, containing largely phenols, hydrocarbons, oils, and paraffines; exhaustion by organic solvents yields a lignite wax similar to that obtained by treating lignites of the Landes or of the Rhenan district. By exhaustion with benzole or other solvents, it is possible to obtain from these lignites 6 or 7 per cent of wax with the following composition:

	<i>per cent</i>
Pure wax.....	58.2
Resin.....	41.8

The Caunette lignite, however, yields a very small amount—about 1 per cent. The results of our experiments are as follows:

Solvent used:	<i>Melting point °C.</i>	<i>Per cent of wax</i>
Benzene.....	86	1.05
Toluene.....	86	0.6
Benzene and alcohol.....	92	1.05

The mixture, toluene and alcohol, has given 4 per cent of a substance, which melts at about 100°, and which is not, therefore, a pure mineral wax. Furthermore, dimethylanilin, the properties of which as a solvent we have disclosed for the first time, gave an extract of 17 per cent; and anilin gave one of 23 per cent.

But these extracts begin to soften at about 115°, are like dough at 150°, and melt almost completely at about 170°. They are then not like mineral wax, the melting point of which is within the range of 75° to 80°.

If this extract is exhausted by acetone, part is dissolved; and we get a solid residue, which is black, brilliant, with conchoidal fracture, and melts at 86° to 87°. It may be electrified by rubbing. It is partially soluble in benzene, and wholly in a mixture of alcohol and benzene. We thus obtain 8 to 9 per cent (in weight) of the lignite treated.

A propyl acetate analysis of this wax by the method we have described, reveals its composition as follows:

	<i>per cent</i>
Wax.....	8-10
Resin.....	92-90

It is, then, a quite different wax from the one which we extracted from the lignites of Lalluque (Landes) of the Rhine district and of Czecho-Slovakia, the latter having given a mineral wax with 29 per cent of resin.

According to the works of Pschorr and Pfaff, the wax of lignite is made up of a mixture of free montanic acid  $C_{28}H_{56}O_2$  and esters of this acid, combined with the following acids: cerylic  $C_{26}H_{54}O$ , myricic  $C_{36}H_{62}O$ , and tetracosanic  $C_{24}H_{50}O$ .

The resin of lignite is, chemically speaking, not well defined. The elementary analysis gives a formula approaching  $C_{24}H_{24}O$ . I have already proved that, if we heat esters of high molecular weight in presence of certain metallic chlorides, they are decomposed. We obtain water, gases, and liquid hydrocarbons (light, middle, and heavy). A similar result is obtained with acids with more than six atoms of carbon.

Lignite wax treated in the same way ought to lead to similar results.

Czecho-Slovakian wax heated with molten zinc chloride furnished gases and liquid products which by fractionated distillation gave:

	<i>Weight grams</i>	<i>D<sub>11</sub></i>
70 to 150 degrees.....	14	0.7608
150 to 200 degrees.....	16	0.7819
200 to 250 degrees.....	24	0.8309
250 to 300 degrees.....	42	0.8514
300 to 350 degrees.....	30	0.8537
350 to 400 degrees.....	28	0.8540
Residue above 400 degrees.....	48	0.8540

These are made up of hydrocarbons of the methane series. We could identify hexane, heptane, octane, and nonane with a certain proportion of ethylenic hydrocarbons and ketones,—the last, by increasing the density of the mixture.

The solid fraction distilling between 350° and 450°, when treated by boiling acetone gives splendid white pearly flakes, melting, after centrifugation, at 49° to 50°. These are composed of hydrocarbons resembling the paraffin waxes.

We had, to sum up, an artificial petroleum.

When we consider the various lignites of the world, we find a very wide range from the xyloid, of the younger age, to the bituminous, certain of which have hydrocarbon contents above that observed among the bituminous coals.

Treatment of French lignites is more difficult, because they are often very rich in sulphur—6 to 7 per cent, and even 12 per cent.

A study of the treatment of lignites should include those of the United States. According to a Report of the Federal Oil Conservation Board, reserves of lignite are estimated at 940 billions of tons, which can furnish 70 billions of barrels of liquid fuel, including 12 billion of light products,—substitutes for gasoline.

It will be necessary to examine the American lignites to see whether they should be treated by a previous distillation, leading to a tar, which should be transformed into light products by suitable methods, such as cracking or hydrogenation; and to a semi-coke, which may be used either as a solid fuel or transformed into gas. It might be better to hydrogenate the lignites directly.

A similar problem must be solved in each country.

## II. LOW TEMPERATURE CARBONIZATION OF COAL

Bituminous coal seems to be the ultimate stage in the evolution of lignite. The bitumen contents vary according to the origin of the coal.

There are very important reserves in most countries of the world. In the United States especially, according to a Report of the Federal Oil Conservation Boards, these reserves are estimated at 2400 billion tons.

By low temperature carbonizing, bituminous coal gives an oil somewhat different from the one obtained from the lignites.

The tar is rich in phenols and acid compounds similar to lignite tars; but that important proportion of solid paraffins which is found in lignite tars is not found in the coal.

As in the treatment of lignite, we prepared low temperature tar by distilling bituminous coals in a current of steam, slightly superheated without exceeding  $480^{\circ}$ , so as to prevent as much as possible, a cracking of the original compounds.

This tar is viscous, black, denser than water; and the semi-coke obtained is very hard.

In order to avoid reaching the temperature at which the products would be decomposed, we did not carbonize these bituminous coals very far; and the coke obtained had still a very large proportion of volatile matter, varying from 12 to 16 per cent, according to the coal treated.

We know that low temperature tars contain oils, which are chiefly composed of hydrocarbon and acid compounds, composed largely of phenols.

Ketonic products and bases are also found.

The primary tar obtained by steam sweeping during distillation is quite similar.

The very large proportion of compounds soluble in alkali is the reason why the separation of these constituents by soda washing is rather impractical and somewhat laborious. Franz Fischer has shown that it was possible to separate higher phenols from hydrocarbons by superheated water. It has also been proposed to eliminate the most important part of the phenols by an initial treatment with milk of lime and a final removal of the last fractions by soda.

We tried to use with coal tar the process of separation of phenols from oils by action of methanol.

To 100 grams of low temperature tar, obtained by carbonization of Bruay coal, we added 100 grams of methanol at 99 per cent ( $d = 0.790$ ). The mixture was then heated to  $40^{\circ}$  to  $50^{\circ}$  for a few minutes. By cooling, it has been possible to separate an oil of higher density than the supernatant alcohol.

We obtained 65 grams of a black, viscous oil, composed chiefly of hydrocarbon (56 to 57 per cent). The alcohol contained largely phenols and compounds soluble in soda, with 7 to 9 per cent of hydrocarbon oils.

It is then possible roughly to separate hydrocarbon and phenols in a low temperature tar.

By forming the sodium compounds, we separated phenols and acids, and studied the solubility of these compounds.

We dissolved 35 grams of acid and phenols in 35 grams of methanol of 99 per cent. The solution was waterwhite and remained unaltered by the addition of 7 grams of water (20 per cent in weight of methanol). We discovered a slight turbidity on adding 5 grams. With 10 grams separation became noticeable; phenols and acids being precipitated.

According to this experiment, we thought, that if phenols were still soluble in methanol to which 20 per cent (by weight) of water had been added, hydrocarbons should perhaps remain nearly insoluble.

We treated 90 grams of crude tar by 100 grams of methanol to which 20 grams of water had been added ( $d = 0.830$ ). The experiment was conducted as previously indicated.

We obtained 56 grams of oil, containing 2 to 3 grams of phenols; and 33 grams of phenols containing 6 grams of oil.

Improvement was apparent for the oil fraction, but was not noticeable for the phenols.

We then studied systematically the separation of hydrocarbons from phenols or acids, by using different mixtures of methanol and water.

Results are summed up as follows:

(1) Methanol ( $d = 0.840$ ):

We treated: Low temperature tar (90 grams) by methanol ( $d = 0.840$ ) 120 grams

We obtained:

58 grams of oil containing 3 grams of phenols

30 grams of phenols containing 4 grams of oils

(2) Methanol ( $d = 0.845$ ):

We treated: Low temperature tar (100 grams) by methanol ( $d = 0.845$ ) 240 grams

We obtained:

Oils containing 3 to 4 grams of phenols

Phenols containing 1.5 to 2 grams of oils

(3) Methanol ( $d = 0.850$ ):

We treated: Low temperature tar (100 grams) by methanol ( $d = 0.850$ ) 200 grams

We obtained:

Oils containing only 1 to 1.5 grams of phenols

Phenols containing 1 to 5 grams of oils

(4) Methanol ( $d = 0.855$ ):

We treated: Low temperature tar (70 grams) by methanol ( $d = 0.855$ ) 120 grams

We obtained:

Oils containing only traces of phenols

Phenols containing 2 grams of oils.

We conducted another experiment with:

Low temperature tar 120 grams, and methanol ( $d = 0.855$ ) 300 grams

We obtained:

Oils containing only slight traces of phenols

35 grams of phenols contained 3 grams of oils

(5) Methanol ( $d = 0.860$ ):

We separated 100 grams of tar into 75 grams of insoluble products, containing 13 per cent of phenols and acids soluble in soda, and 25 grams of phenols recovered by evaporation of the alcohol, containing 0.3 gram of hydrocarbon oils.

We find that in a methanol-water mixture of the density of 0.860 phenols begin to become noticeably insoluble.

We then conclude that it is necessary to use a mixture of a density between 0.850 to 0.855, to obtain a serviceable separation of hydrocarbons and phenols or acids of the primary tar. With such a solution we found that oils obtained had only traces of phenols and that the phenols carry 1.5 grams of oils. The most suitable quantity of mixture to be used seems to be 180 to 200 grams of the mixture to 100 grams of tar.

A Durham coal (Denaby) furnished by this method, 70 grams of oils containing practically no phenols and 30 grams of phenols with 1.8 to 2 per cent of oils.

One hundred sixty grams of Denaby tar gave by the same process, when treated by 320 grams (twice the weight of tar) of methanol,  $d = 0.850$ , gave oils with traces of phenols and phenols at 2 per cent of oils.

Polish "Robur" coal gave 70 per cent of oils, without phenols, and 30 per cent of phenols at 2.5 per cent of oils.

If the quantity of mixture ( $d = 0.850$ ) is smaller, preceding results

are not reached: 100 grams Denaby tar, for instance, treated by  $1\frac{1}{2}$  its weight of methanol mixture ( $d = 0.850$ ) gave 70 grams of oils containing 4 grams of phenols and 30 grams of phenols containing 6 grams of oils.

Other results obtained with Polish coal ("nuts" of Robur)

- (a) 100 grams tar treated with 200 grams methanol ( $d = 0.850$ ):
  - 70 grams of oil with 1.5 grams phenols
  - 30 grams of phenols with 0.5 gram of oils
- (b) 110 grams tar treated with 220 grams methanol ( $d = 0.850$ ):
  - 74 grams of oils with 2 grams phenols
  - 32 grams of phenols with 2.5 grams of oils
- (c) 150 grams of tar treated by 300 grams of methanol ( $d = 0.850$ ):
  - 105 grams of phenols with 1 gram 7 of oils
  - 45 grams of oils with 1 gram of phenols

We find then that we have a very easy method of separating oils from phenols in low temperature tars. Methanol may of course be recovered by distillation; the losses should generally not exceed 2 per cent.

In addition, we must point out that it is not necessary to dehydrate the tar previously. It is sufficient to determine its water content and to take account of this in preparing the mixture of methanol and water of the required proportion.

Treatment of lignite tars by a counter current of 90 per cent ethanol is industrially used at Zeitz (Saxony). A very satisfactory separation of oils and phenols is obtained.

We studied how ethanol acts with low temperature coal tar.

Ninety-five per cent ethanol,  $d = 0.790$ , dissolves nearly all oils and all phenols and it is then useless for separation of these two classes of compounds.

We made systematic researches so as to find the proper mixture of water and ethanol leading to the best separation of hydrocarbons from acids and phenols.

Here are the results obtained with nuts of Polish Robur coal.

- (1) 90 per cent ethanol ( $d = 0.840$ ):
  - Low temperature tar 100 grams
  - Treated by ethanol ( $d = 0.840$ ) 200 grams
  - We obtained:
    - 65 grams of oils containing 2.5 grams of phenols
    - 34 grams of phenols containing 5 grams of oils

- (2) 86 per cent ethanol ( $d = 0.850$ ):  
(a) Low temperature tar 100 grams  
Treated by ethanol ( $d = 0.850$ ) 200 grams  
We obtained:  
68 grams of oils containing 2 grams of phenols  
32 grams of phenols containing 5 grams of oils  
(b) Low temperature tar 130 grams  
Treated by ethanol ( $d = 0.850$ ) 260 grams  
We obtained:  
82 grams of oil containing 0.5 gram of phenols  
48 grams of phenols containing 8.5 grams of oils
- (3) 84 per cent ethanol ( $d = 0.855$ ):  
Low temperature tar 260 grams  
Treated by ethanol ( $d = 0.855$ ) 520 grams  
We obtained:  
200 grams of oils containing 2 grams of phenols  
70 grams of phenols containing 3 grams of oils
- (4) 82 per cent ethanol ( $d = 0.860$ ):  
Low temperature tar 100 grams  
Treated by ethanol ( $d = 0.860$ ) 200 grams  
We obtained:  
70 grams of oils, containing less than  $\frac{1}{2}$  gram of phenols  
31 grams of phenols containing 2 grams of oils
- (5) 78 per cent ethanol ( $d = 0.870$ ):  
Low temperature tar 80 grams  
Treated by ethanol ( $d = 0.870$ )  
We obtained:  
Oils containing 1 gram of phenols  
Phenols 3 grams

A British coal sample (Denaby-Durham) led to the following results:

- (1) 86 per cent ethanol ( $d = 0.850$ ):  
Low temperature tar 80 grams  
Treated by ethanol 160 grams  
We obtained:  
45 grams of oils, containing 0.5 gram of phenols  
35 grams of phenols containing 12 grams of oils
- (2) Low temperature tar 100 grams  
Treated by ethanol ( $d = 0.850$ ) 200 grams  
We obtained:  
62 grams of oils, containing but traces of phenols  
38 grams of oils and phenols which have been submitted to a second treatment with 200 grams of ethanol ( $d = 0.855$ ), we obtained from the second fraction:  
12 grams of oils containing 2 grams of phenols  
26 grams of phenols containing 3 grams of oils

The first treatment gave a sensibly pure oil, without phenols, and phenols without a large proportion of oils; the second treatment gave mixtures of both series.

Those results prove that a good separation of oils and phenols may be reached by using ordinary ethanol ( $d = 0.860$ ); that is  $82^\circ$  ethanol. For degrees comprised between  $82^\circ$  and  $85^\circ$  and  $78^\circ$ , separation of oils from phenols is also sufficient.

We have also foreseen the use of isopropylic alcohol which is today a by-product of the treatment of cracking gases or of petrol catalysis.

The treatment of 100 grams of tar with 200 grams of isopropylic alcohol ( $d = 0.850$ ) gave 50 grams of oils containin but traces of phenols, and 50 grams of phenolic or acid compounds which are separated by distilling the solvent.\* Those products contain 15 to 18 grams of oils.

- (a) 100 grams of tar treated by 200 grams of isopropylic alcohol ( $d = 0.850$ ) gave 45 grams of oils with traces of phenols and 55 grams of phenols containing 24 grams of oils.
- (b) By treatment with isopropylic alcohol ( $d = 0.870$ ), we obtained 65 grams of oils containing 2 grams of phenols and 35 grams of phenols containing 9 grams of oils.
- (c) By treatment with isopropylic alcohol ( $d = 0.872$ ), we obtained 67 grams of oils, containing 1 gram of phenols and 34 grams of phenols containing 6 grams of oils.
- (d) 120 grams of low temperature tar treated by 200 grams of isopropylic alcohol ( $d = 0.865$ ) gave 74 grams of oils without the slightest appreciable trace of phenols and 46 grams of phenols containing 10 grams of oils.

Isopropylic alcohol permitted then, the separation of an oil containing an exceedingly small amount of phenols, from phenols containing a somewhat higher proportion of oils.

The conclusion of this work is that methanol and ethanol, sufficiently diluted, are excellent solvents for separating oils from phenolic and acid compounds of low temperature tar.

A slight soda washing of the oils leads to oils quite free from phenols.

In the study of low temperature phenols, it is possible to utilize sodic salt, in order to eliminate traces of oils. But it may happen that in most of the cases of industrial practice that treatment will be absolutely useless. If a further transformation of oils be required, it is more advantageous to start from products nearly completely free from phenols.

In the following researches, we always fully purified all obtained products.

We do not intend to discuss here all researches made on oils and phenols of low temperature tar. We shall recall those of Bergius on the hydrogenation of primary coal; of Franz Fischer and Schrader on the transformation of phenols into aromatic hydrocarbons, and on the destructive distillation of the tar. It shows what interest lies in this new product.

We shall only describe a few experiments on the catalytic transformation of those various compounds.

### 1. Oils

Oils of the low temperature tar obtained by distillation of coal in a current of slightly superheated steam are black and thick. Their density falls between 1.03 and 1.08. The starting point of distillation is at about 150°, but under 250° we obtain only 7 per cent of light oils. Light products belong to the three series: aromatic, paraffinic, and ethylenic. The middle products are mostly aromatic.

We treated the oils by different catalytic agents either in liquid phase or in vapor phase.

*a. Catalysis in liquid phase. Aluminum chloride.* Treatment of vacuum tar by aluminum chloride studied by Pictet and Melle Leczinska in 1916.<sup>1</sup> Fractions distilling above 200° have been given.

	<i>per cent</i>
Distilling under 140 degrees.....	15
Distilling between 140 and 180 degrees.....	30
Distilling above 180 degrees.....	35

Oils of low temperature tar heated with aluminum chloride led to a series of light and heavy products and also to a pitch, which remained mixed with the chloride.

	$D_{15}$	$n_D^{20}$
60 to 150 degrees.....	0.7919	1.4325
150 to 200 degrees.....	0.8412	1.4625
200 to 240 degrees.....	0.8782	1.4937
240 to 260 degrees.....	0.9106	1.4937

Light fractions 60° to 150° and 150° to 200° contain chiefly saturated and aromatic hydrocarbons. In the first fraction we could identify

<sup>1</sup> Bull. Soc. Chim., 247, p. 329, 1916.

positively, metaxylene by its trinitrated derivate, which crystallizes into splendid needles, with a melting point of  $176^{\circ}$ .

*Ferric chloride* ( $Fe Cl_3$ ). It does not react well with low temperature oils.

*Chloride of zinc*. When we heat low temperature oils with dry or molten zinc chloride we observe a slow and regular distillation, which leads to the following fractions:

	$D_{20}$	$n_D^{25}$	Per cent absorbable by methylsulphate
Below 200 degrees.....	0.8261	1.4626	68
200 to 240 degrees.....	0.8773	1.4925	60
240 to 270 degrees.....	0.9103	1.5179	52
270 to 310 degrees.....	0.9345	1.5340	48

Action of methylsulphate shows the aromatic and ethylenic character of the products.

From about the middle of the operation until the end, there is formed also a gas with the following composition:

	per cent
$CO_2$ .....	0.6
$C_nH_{2n}$ .....	2.1
CO.....	0.4
$CH_4$ .....	4.8
$H_2$ .....	86.0
$N_2$ .....	5.1

*Stannous chloride*. By distilling low temperature tar with stannous chloride, we obtain also a liquid, which by distillation gives following fraction.

	$D_{20}$	$n_D^{25}$	Per cent soluble in methylsulphate
Below 200 degrees.....	0.8551	1.4831	60
200 to 250 degrees.....	0.9026	1.5127	60
250 to 300 degrees.....	—	1.5275	60
Above 300 degrees.....	0.9620	1.5500	52

It is similar to the liquid obtained with the chloride of zinc; and the gas escaping during the reaction has a nearly identical composition:

	per cent
$CO_2$ .....	0.4
$C_nH_{2n}$ .....	2.4
CO.....	0.1
$CH_4$ .....	4.8
$H_2$ .....	86.7
$N_2$ .....	4.6

*b. Catalysis in vapor phase.* When we send the vapors of low temperature tar oils in a copper tube containing copper scraps, we obtain from 400° up a very sensible decomposition of those oils into light products, with production of a gas burning with a luminous flame.

The decomposition is more active, if we heat to 500° to 530°. The analysis gave the following composition of the gas:

	At 460° per cent	At 530° per cent
CO <sub>2</sub> .....	2.2	6.1
CO.....	7.8	3.1
C <sub>n</sub> H <sub>2n</sub> .....	24.6	26.1
C <sub>n</sub> H <sub>2n + 2</sub> .....	37.5	48.2
H <sub>2</sub> .....	19.8	8.6
O <sub>2</sub> .....	1.1	1.25
N <sub>2</sub> .....	6.8	6.05

If we bubble this gas into bromine water, we obtain quickly a decoloration, owing to the fixation of ethylenic hydrocarbons. Dibromides distil from 130° to 170° and are constituted chiefly of ethylene, propylene, butylene, and amylene bromides. We then obtain all ethylenic hydrocarbons from the second to the fifth term of the series during catalytic decomposition of low temperature oil.

The liquid obtained after treating the tar with diluted sulphuric acid so as to remove basic compounds of a pyridic nature, and with diluted soda so as to remove traces of phenols, gave the following fractions on distillation:

	Quantity parts	D <sub>20</sub>	n <sub>D</sub> <sup>25</sup>
65 to 120 degrees.....	1	0.7803	1.4365
120 to 150 degrees.....	1	0.8063	1.4558
150 to 180 degrees.....	1	0.8362	1.4724
180 to 200 degrees.....	2	0.8737	1.4938
200 to 220 degrees.....	2	0.9040	1.5128
220 to 240 degrees.....	2	0.9282	1.5288
240 to 260 degrees.....	2	0.9516	1.5450

Those densities are very high. The fraction 150° to 200° treated by the sulphonitric mixture can be nearly fully nitrated. The nitrated product exhausted by ether, gives a white powder melting at 215°. It is dinitrobenzene dicarbonic acid—1.3 C<sub>6</sub>H<sub>2</sub>(NO<sub>2</sub>)<sub>2</sub>-(CO<sub>2</sub>H)<sub>2</sub>.

Etheric solution gives a viscous nitrated derivate.

The superior fractions, treated with boiling chloride of aluminum,

give a liquid which by fractionation furnishes a light product, made of paraffinic, cycloparaffinic, and aromatic hydrocarbons,—the aromatics of which could be nitrated by the sulphonitric mixture.

In presence of scraps of nickel and in vapor phase, we obtained products similar to the ones obtained with copper:

	$D_{20}$	$n_D^{25}$	<i>Per cent soluble in methylsulphate</i>
Below 200 degrees.....	0.8598	1.4882	95
200 to 250 degrees.....	0.9180	1.5242	72
250 to 300 degrees.....	0.9840	1.5500	84
300 to 350 degrees.....	1.0360	1.5500	90

Those reactions prove that catalytic decomposition of low temperature tar oils gives, besides cyclic and aliphatic hydrocarbons, a certain percentage of light aromatic hydrocarbons.

## 2. Phenols

We are not well informed on the nature of phenols and soda soluble products, which may be found in low temperature tar. Although cresols and xylenols are identified, we do not know much about the higher phenols. According to Wendel, there should be unsaturated phenols and derivatives with several oxhydriles. They can be found chiefly in fractions boiling above 240°. Marcusson and Picard have found also acids, neutral resins, and small quantities of alcohols. By action of heat, acids give carbon dioxide and liquid paraffins. They found also in primary tars industrially obtained, compounds which were identified as lacton-acids. Several authors think that phenols of primary tars result chiefly from the destruction of asphaltic products.

Phenols distilling below 250° are composed chiefly of cresols and xylenols. There remain above that temperature, viscous compounds, with acid reaction the nature of which we do not understand.

We tried to decompose those products in presence of chloride of zinc; 100 grams of phenolic viscous products boiling above 250° were treated by 15 grams of dried or molten chloride of zinc.

When heating, we obtained a regular distillation of fluid liquid products and of water, which may be easily separated by a rapid reaction.

We obtained 35 per cent of liquid products and a residual coke. When liquids are treated by diluted soda, part is dissolved; and part floats above the soda solution.

This latter part is made up of oils distilling between 100° and 300°. By rectification, we obtained the following fractions:

	$D_{20}$	$n_D$
100 to 200 degrees.....	0.8748	1.4940
200 to 250 degrees.....	0.9641	1.5500
250 to 300 degrees.....	0.9251	1.5500
300 to 330 degrees.....	1.0700	1.5500

These oils are similar to the cracked oils obtained in the presence of copper.

The fraction soluble in soda is regenerated by addition of hydrochloric acid. By this process a liquid with a strong phenolic odor boiling from 205° was separated and from that temperature up to 240° we obtained an important fraction.

By careful rectification of this fraction, we obtained:

	<i>Quantity parts</i>	$D_{19}$	$n_D^{26}$
195 to 198 degrees.....	1	1.034	1.5380
198 to 205 degrees.....	2	1.034	1.5392
205 to 212 degrees.....	2 $\frac{1}{4}$	1.026	1.5365
212 to 220 degrees.....	2 $\frac{1}{4}$	1.021	1.5375
220 to 230 degrees.....	1	1.019	1.5368
230 to 240 degrees.....	1 $\frac{1}{2}$	1.020	1.5386

The above densities and refraction indices correspond about to the characteristics of the 3 cresols and of the xyenols. We could identify the metacresol by its phenylurethane, melting at 122°; the paracresol by its phenylurethane melting at 110°; and the metaxyl-enol 1.3 by its phenylurethane, melting at 103°.

We see that acid products soluble in soda distilling below 250° may give by decomposition with chloride of zinc:

1. Hydrocarbon oils.
2. Phenols among them we could identify meta and paracresol and one metaxyl-enol.

In this reaction, which occurs with elimination of water, gas escapes, the composition of which is as follows:

	<i>per cent</i>
CO <sub>2</sub> .....	1.4
C <sub>n</sub> H <sub>2n</sub> .....	1.6
O <sub>2</sub> .....	0.4
CO.....	0.8
CH <sub>4</sub> .....	11
H <sub>2</sub> .....	82
N <sub>2</sub> .....	2.8

## CONCLUSIONS

From all the above experiments, we may conclude:

1. That we may easily obtain low temperature tar by distilling lignites or coal at temperatures below  $460^{\circ}$ ; in presence of a small quantity of superheated steam reaction occurs more easily, and tar obtained is of a very good quality.

2. That distillation of bituminous lignites give oils, phenols and paraffins; phenols lose the most important part of their sulphur if treated by stannous chloride.

3. That in low temperature tar obtained from bituminous coal, we may easily separate hydrocarbon oils, containing certain chemical compounds, from phenols and acid compounds soluble in soda, by action of methanol, ethanol, or even isopropanol.

4. That methanol and ethanol giving the best results have a density—at ordinary temperature, of 0.850 to 0.855 for methanol, 0.860 for ethanol.

5. That hydrocarbon oils are decomposed in the presence of certain catalytic agents, either in liquid phase or in vapor phase and that we obtain all products from the lightest to the heaviest.

6. That phenolic or soda-soluble compounds obtained from low temperature tar and distilling above  $250^{\circ}$  (free from cresols and xylenols), when distilled in presence of chloride of zinc, are decomposed and give phenols with low boiling points (cresols, xylenols) and hydrocarbon oils distilling within the range  $100^{\circ}$  to  $350^{\circ}$ . We can thus obtain a new proportion of useful phenols and of light and heavy hydrocarbons.

Most of these experiments have not been disclosed until the present time.

# CONTINUOUS DISTILLATION OF COAL TARs AND CRUDE OILs BY SUPERHEATED STEAM

## "THE AB-DER-HALDEN PROCESS"

By J. V. HENRI WINKLER

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At the present time crude mineral oils or tars obtained by distilling coal, lignites or schists at high or low temperature cannot be used in the crude state except as liquid fuels.

On the other hand, by proper treatment, we can extract from these minerals oils or crude tars a whole series of products capable of a great variety of uses and of considerable commercial value.

This "conversion" of crude tars or mineral oils into useful products is, at the present time, the order of the day and constitutes one of the industrial problems most studied.

We may say, without danger of committing too great an error, that all the industrial treatment which all these substances undergo have, as a starting point, a preliminary distillation.

On this first operation depends, in many cases, all future treatment, as well as the commercial value of the products obtained.

One can readily see that a slow process of distillation with superheating of crude products can be used whenever one desires to crack the oils to extract gasoline. To obtain lubricating oils there should be used a process of vacuum distillation with or without steam injection.

In other cases, bad fractionation, at the time of the first distillation, requires, during treatment, numerous rectifications or redistillations which would increase the cost considerably.

It follows from what has been said that it is of capital importance to choose wisely from the different processes of distillation, according to the raw material to be treated and the kinds of products one wishes to obtain.

The aim of my paper is not to explain to you the different processes of distillation which have found an industrial application, not to point out their defects or their advantages, but rather to focus your attention on the Ab-der-Halden system—still unknown in the United States, but which has proved its value in Europe—and which

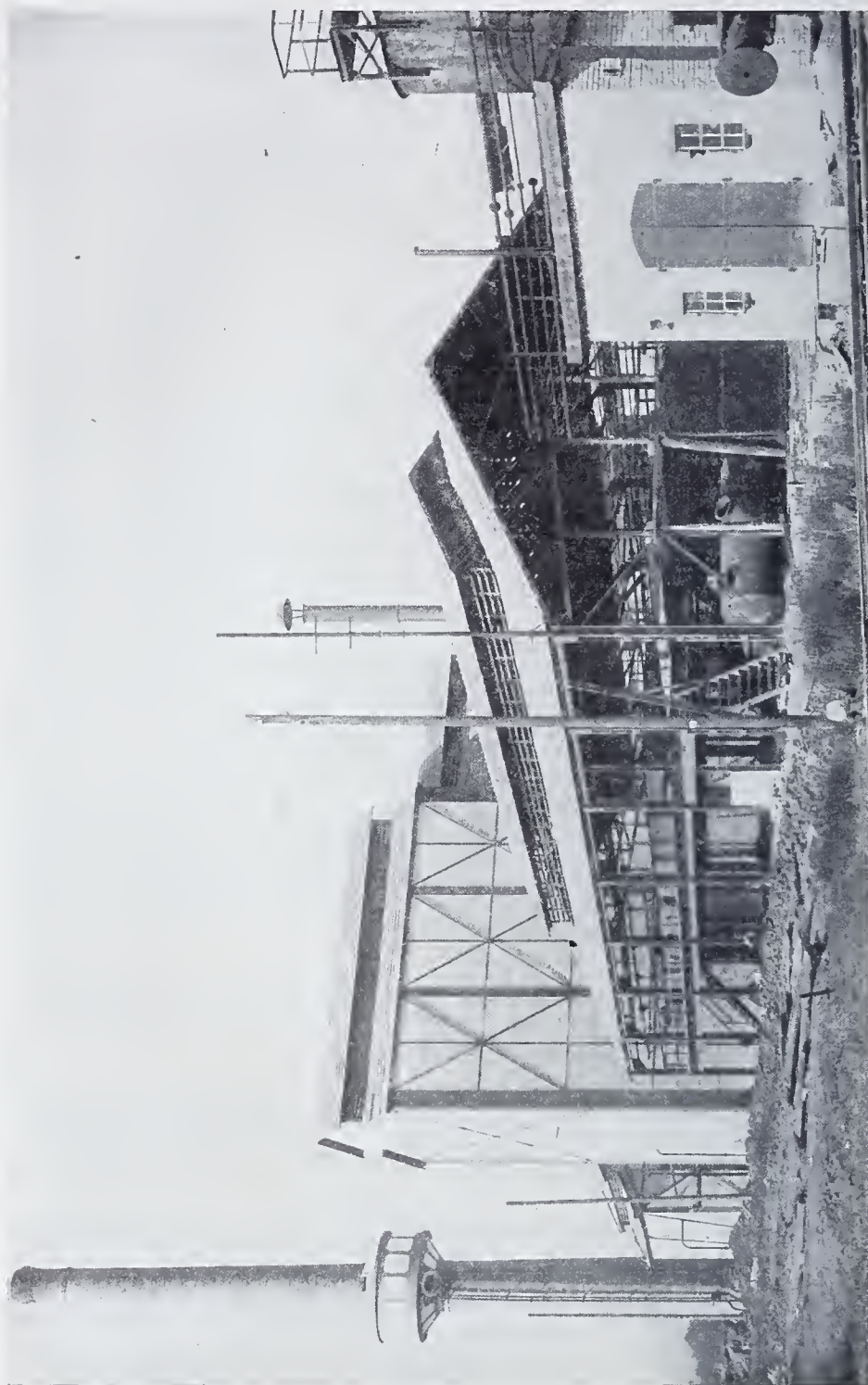


FIG. 1. VIEW OF A TAR DISTILLERY AB-DER-HALDEN SYSTEM

seems to constitute one of the most important improvements effected in the tar industry.

We owe this process to the remarkable researches of M. C. Abder-Halden who has overcome all difficulties by making use of the known

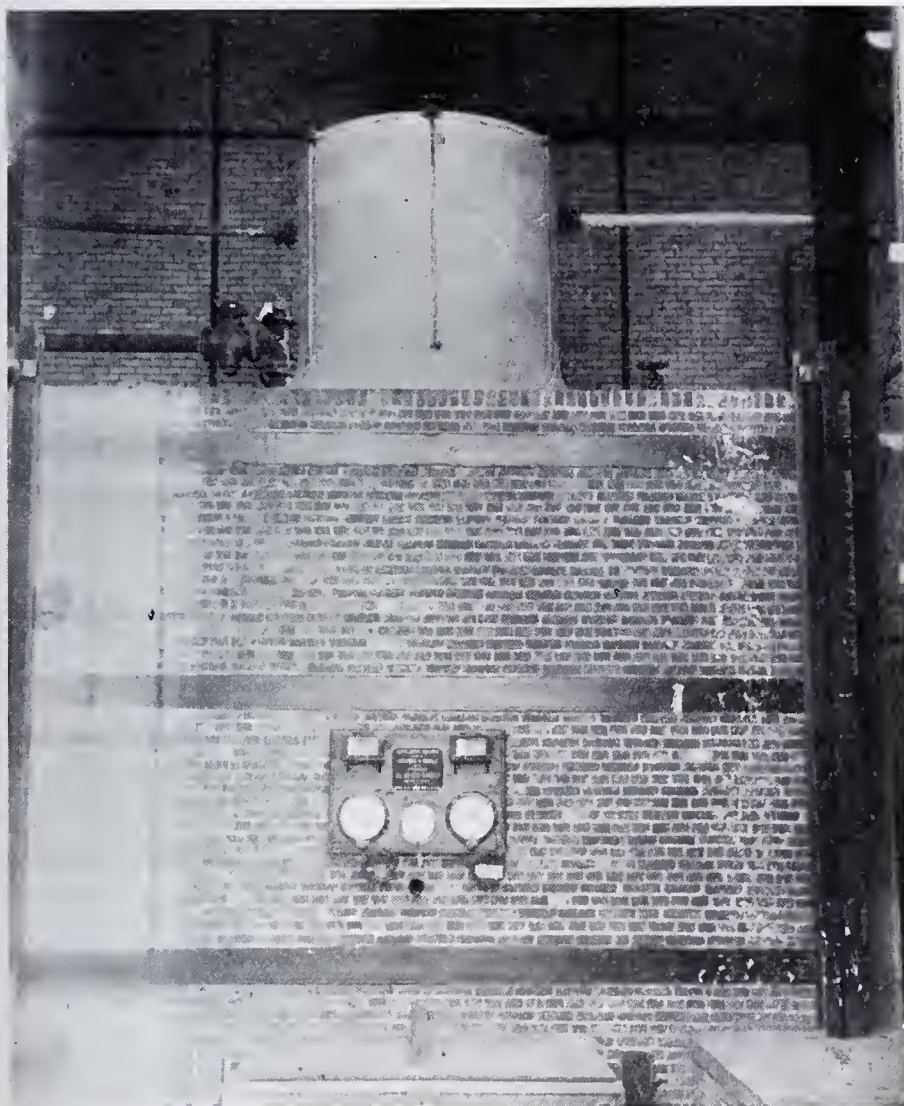


FIG. 2. CONTINUOUS DISTILLATION RETORT. CAPACITY 60 TONS PER 24 HOURS

property which superheated steam possesses in carrying over the hydrocarbons at a lower temperature than their boiling point.

In fact, this property permits us to lower the temperature of dis-

tillation and consequently to do away with cracking and to fractionate rigorously the by-products as we shall see presently.

It must be mentioned finally, that tars and crude mineral oils usually contain a considerable quantity of water, which usually causes a very persistent emulsion when heated to a temperature above  $100^{\circ}\text{C}$ ., so that the distilling process itself must be preceded by dehydration effected by physical or thermal processes.

The Ab-der-Halden process has the advantage of doing away with this inconvenience.

### PRINCIPLE OF THE AB-DER-HALDEN PROCESS

The laws upon which the Ab-der-Halden process is based are those which govern the distillation of a mixture of two non-miscible liquids.

Dalton was first to point out a law which may be stated as follows:

I. "When a liquid is contained in a vessel with air or any other gas or vapor that has no chemical action upon it, the amount that will evaporate and the pressure of its saturated vapor will be the same as though the other gas were not there, and the total pressure will be the sum of the pressures of the gas and of the saturated vapor."

By replacing the gas with a saturating vapor, this law leads to the following law verified by Regnault:

II. "The vapor pressure of a mixture of two non-miscible liquids is equal to the sum of the vapor pressures of each of the two liquids."

Experience shows that this law is not applicable to miscible liquids, that it becomes almost exact in the case of non-miscible liquids.

As a consequence of the latter law, if we observe that in a given volume the number of molecules of one of the vapors of the mixture is proportional to the particular pressure of this vapor, we can foresee the following law:

III. "The number of molecules of each of the liquids distilling at the same time is proportional to the vapor pressures of each of the two liquids at the boiling temperature of the mixture."

This law has been verified by Naumann who has found the figures reproduced in Table I.

From the second law it follows that for a mixture of water and tar, the vapor pressure of the mixture will be the sum of the vapor pressure of the water and the vapor pressure of the tar.

At a temperature of  $100^{\circ}\text{C}$ . the vapor pressure of the mixture will be greater than the atmospheric pressure and boiling will take place before reaching this temperature.

But if it is possible to obtain distillation under 100°C. on the contrary, the amount of tar vapor which will pass over will be very small by application of the third law, since the vapor pressure of tar in the neighborhood of 100°C. is much lower than the vapor pressure of water.

The quantity of water necessary becomes so great as to prohibit all industrial application.

The experiments of Mr. Charles Ab-der-Halden have given, for a mixture of water and definite fractions of tars, the results shown in Table II.

TABLE I

HYDROCARBONS	BOILING POINT		PRESSURE	RATIO MOLEC. WATER MOLEC. BODY	RATIO TENSION WATER TENSION BODIES
	Of pure body	Of mixed vapor			
	<i>degrees</i>	<i>degrees</i>	<i>mm</i>		
Benzene.....	79.5	69.1	742	0.41	0.42
Toluene.....	108.5	84	752	1.27	1.26
Naphthalene.....	218	98.8	750	39.90	36.40

TABLE II

BOILING TEMPERATURE OF FRACTION EXAMINED	AVERAGE TEMPERATURE OF DISTILLATION OF MIXED VAPORS	VOLUMES DISTILLING AT THE SAME TIME		QUANTITY OF WATER NECESSARY TO CARRY OVER 100 CC. OF OIL
		Oil	Water	
<i>degrees</i>	<i>degrees</i>			<i>grams</i>
50-100	75	14	7	50
150-200	95	9	21	233
200-250	98	15	130	866
250-300	99	3	114	3.800
300-350	99.5	1	115	11.570

But if instead of distilling a mixture of water and tar we allow to pass through the tar, which can be heated above 100°, superheated steam, the first law permits us to foresee that the quantity of tar vapor which will mix with steam will be greater than that contained in the mixed vapor coming from the distillation of water tar mixture. In fact the tar can thus, in steam, emit vapors until the pressure of the emitted vapors is equal to the vapor pressure of the tar at the temperature at which one is working.

Experience has proved this to be correct. Thus we succeed in reducing considerably the quantity of water necessary to distill tar.

The process, which is the subject of my lecture, is based upon the following principle which can be stated thus:

"The distillation of crude tar, with superheated steam permits us to separate all the volatile substances by leaving a residue of pitch whose characteristics depend on the temperature of the distillation.

"On this temperature of distillation depends the ratio of steam to oil vapor; we can assume that this temperature can be fixed at 300° in order that the quantity of steam does not exceed 40 to 50 per cent of the weight of the tar distilled, a quantity which is industrially practical."

It is here that it must be pointed out that the Ab-der-Halden process operates inversely to the ordinary systems of distillation which heat the coal tar gradually and collect the heavier and still heavier fractions.

By the Ab-der-Halden system, on the contrary, we can extract almost instantaneously all the volatile oils and then separate them by fractional condensation, leaving only pitch in the distilling retort.

The same laws govern also fractional condensation.

By subjecting a mixed vapor of oil and water to a gradual lowering of temperature, we can extract at each step a determined fraction of oil, the only one that can exist in the liquid state at the temperature of this step in the presence of steam. It is thus that by cooling the water-oil vapors of coal tar to a temperature of 170° we can condense a fraction containing practically all the anthracene whose pressure is negligible at this temperature; on the contrary the naphthalenic oils remain in the vapor state since at this pressure the vapor pressure of naphthalene is considerable.

#### INDUSTRIAL REALIZATION

Since continuous distillation of coal tars from coke ovens or gas works presents specific difficulties, encountered in a much lesser degree in the crude oils industries, I shall begin my explanation by pointing out the industrial realization of the Ab-der-Halden system when applied to coal tar.

In fact it is to be noted that the greatest portion of by-products derived from coal tar such as: naphthalene, anthracene, etc., are solid at ordinary temperature.

Moreover, the residue of distillation (pitch) amounts to 50 to 60 per cent, and is made up of substances decomposing easily at a temperature of 400°, leaving a coke deposit on the walls of the apparatus, and thus preventing heat transmission.

Another difficulty presents itself in the rigorous fractioning of the different oils, due to their physical properties.

It is thus that the aromatic hydrocarbons such as naphthalene, remain in solution in the oils which accompany them at a higher temperature than their boiling point.

In a pure state the boiling point of naphthalene is  $218^{\circ}$ ; when it is mixed with tar oils it distills between  $250$  and  $270^{\circ}\text{C}$ .

The Ab-der-Halden process consists of two distinct phases.

First, the separation of coal tar into pitch and a mixture of oil and water vapors.

Second, the fractioning of the mixed vapors.

I will now describe the apparatus used by the Societe "Huiles, Goudrons et Derives" de Lens, which assures at the present time the annual treatment of 60,000 tons of tar.

The general arrangement is shown by the diagram (Fig. 3).

The crude tar is received through a pump with an adjustable flow (1) which feeds the tar first into a preheater (2) where it is reheated on coming in contact with the hot pitch issuing from the retort. Its temperature rises to  $70^{\circ}$ , then it passes into a reheater (3) made up of a tubular bundle arranged in the flues of the retort.

This apparatus raises the temperature of the tar to over  $100^{\circ}$  and causes the evaporation of the water it contains so that a mixture of hot tar and water vapor, which results from the dehydration of the moist tar, enters the retort.

This mixture is introduced into the mass of pitch remaining in the retort at the same time as the superheated steam necessary for the carrying over of the oils. This retort is kept at a temperature of  $290^{\circ}$  to  $300^{\circ}$  depending on the quality of the pitch desired.

Under the influence of the superheated steam, the tar is distilled almost instantaneously. The oil and water vapors issue from the retort, while the pitch, as it forms, flows out continuously by means of a spillway. It passes into the preheater where it cools to about  $200^{\circ}$ , then on into the stock reservoir.

This arrangement does away with the disadvantages resulting from dehydration of tar; in fact, the water, having vaporized in the reheater, reaches the retort in a vapor state and helps in the carrying over of the oils in the same way as the injected steam.

The mixed vapors of oil and water are fractionated in a device having two columns working in series, both being equipped with a dephlegmator which permits of regulating the temperature of the



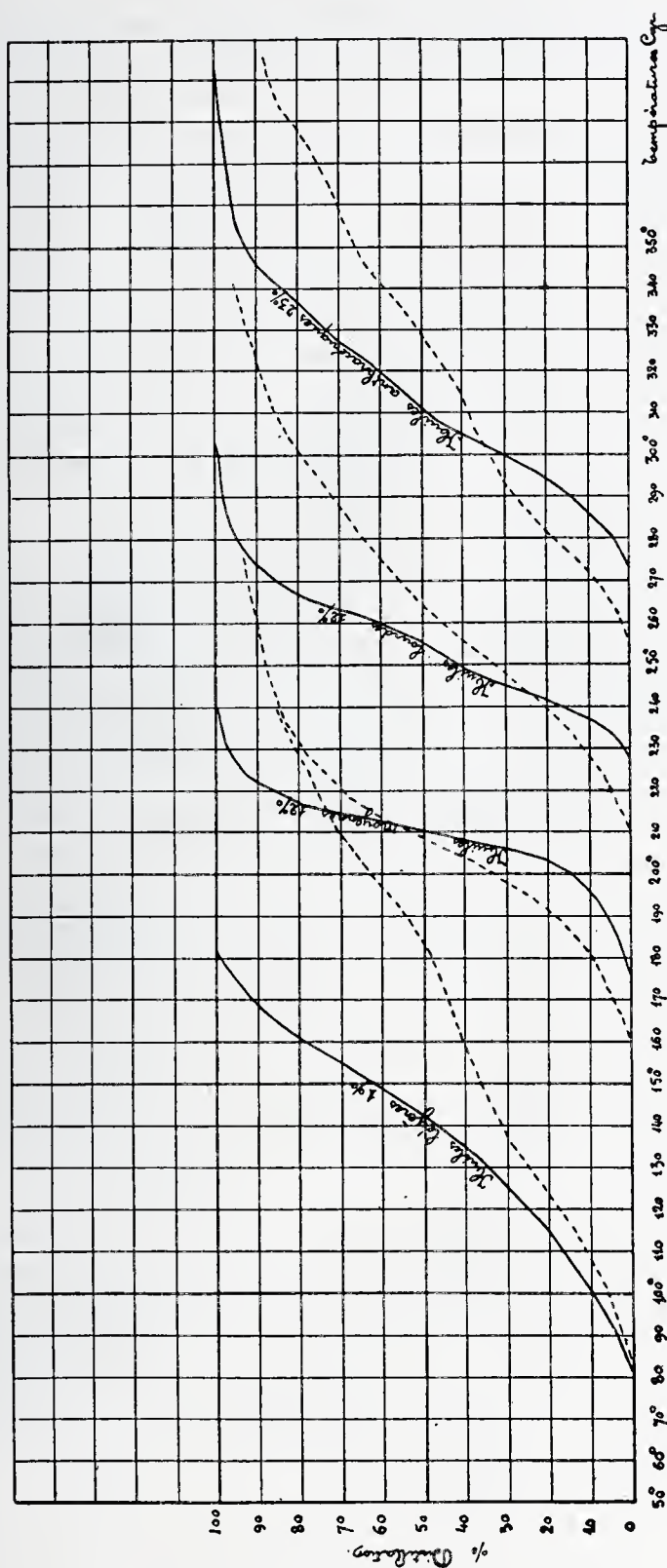


FIG. 4. FRACTIONAL CURVES FOR COAL TAR FROM THE COKING PLANT OF PAS-DE-CALAIS

distillates. Thus, at the base of each column is collected an oil whose composition is governed rigorously by the controlling temperature.

In general, column (5) separates the anthracene oil boiling between 280° and 360°C. and containing all of the anthracene; column (6) removes the heavy oil boiling between 230° and 280° and containing no anthracene or naphthalene. The vapors issuing from column (6) still contain all of the water injected in the form of steam and contained in the crude tar as well as the naphthalene and light oils.

These vapors reach a water condenser (7) which condenses almost completely the injected steam, together with the naphthalene oil. The temperature of this apparatus is regulated in such a way as to allow only the light oil vapors to escape which are rectified in column (8) and finally condensed in condenser (9).

The naphthalene oils and the light oils are separated from the condensed water simultaneously in two separating funnels (10 and 11).

The device I have just described allows us to regulate the composition of each product and to obtain all the desired characteristics. Moreover, this control is independent of the operation of the retort whose object is to separate the pitch, but which cannot have any influence on the fractioning of the vapors. This special feature simplifies operations, contrary to the operation of other apparatus having a retort for the products to be separated.

The preceding diagram (Fig. 4), gives fractionation curves obtained directly from a coal tar obtained from the coking plant of Pas-de-Calais, as well as the proportions of each of the products obtained.

For comparison, the corresponding fractionations obtained have been drawn in dotted lines.

After this account of the industrial realization of the Ab-der-Halden process, in so far as it concerns coal tars of coke ovens and gas works, I shall pass to the application of the process to primary tars.

#### TREATMENT OF PRIMARY TARS

The composition of tars obtained by distilling coal at low temperature is quite different from that of coking plants.

The first, in fact, can be distinguished by an almost total absence of aromatic hydrocarbons, such as benzene, naphthalene, anthracene, etc., moreover, they have a lower pitch content and contain, above all, a great quantity of bodies having phenolic functions.

The majority of these phenolic products, with the exception of the lighter compounds, have not found, to date, a use which would justify their extraction.

It remains to be stated that the water content of these tars, in general, is very high.

The following diagram (Fig. 5) shows the arrangement of the apparatus which permits the continuous distillation and fractionation of crude tars along with the recovery of phenols.

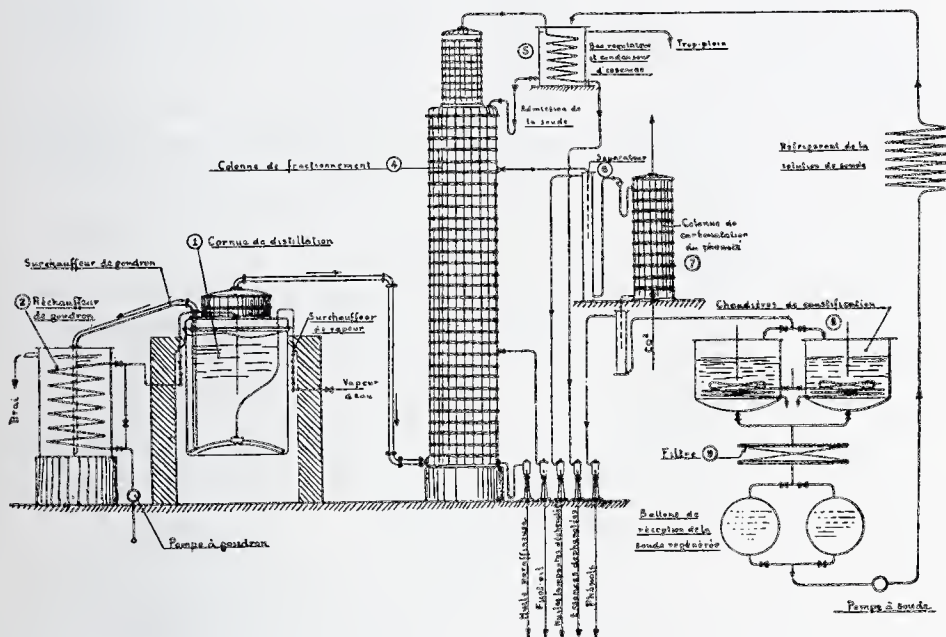


FIG. 5. ARRANGEMENT OF APPARATUS FOR CONTINUOUS DISTILLATION OF TAR AND RECOVERY OF PHENOLS

On the whole there is no great difference between the Ab-der-Halden system for primary tars and the one we have just examined for tars of gas works or coke ovens, with the exception of a special device which permits us to recover the most valuable phenolic compounds.

In this case, the fractionation of the mixed vapors of tar and water is brought about in a single rectifying column equipped at different heights with devices which permit the drawing off of the condensate and prevent its refluxing.

By means of a very close contact between vapor and liquid we obtain by this process a thorough fractionation so that the products

separated at different heights comply at once with commercial requirements.

The extraction of phenol may be brought about by injecting diluted caustic soda at the top of the column and extracting it again at a lower level.

This injection of caustic soda, moreover, brings about an intense cooling of the vapors and permits, at the same time, the complete condensation of steam.

The oil fraction condenses at 100° in the presence of steam and is made up of the products whose boiling points range up to 250°C. and contains all the usable phenols.

On the other hand, the injected caustic soda acts on the phenol more energetically than it does on the oil vapors while condensing them.

The recovery of these phenols and the regeneration of the soda can be done by classic processes.

The warm solution of phenolate of soda on coming out of the column passes into a separator (6) then into a saturator (7) where the decomposition of the phenates is brought about by carbonic acid, thus setting free the phenols.

The carbonate of soda formed is causticized by lime in apparatus (8) and once again returns into the circuit, after preliminary separation of the carbonate of lime in filter (9).

The treatment of primary tars by the Ab-der-Halden process does not present any particular difficulties, and permits of separation, in a single operation, of all the commercial products, such as, gasoline, kerosene, fuel-oil, paraffin oil, pitch and phenols.

We have only to mention now the application of the Ab-der-Halden process to mineral oils.

#### TREATMENT OF CRUDE MINERAL OILS

It may be seen from what has preceded that the application of the Ab-der-Halden process to crude mineral oils will not present any special difficulty. However, it should be mentioned that this process reduces considerably the total treatment and requires at the most one or two operations; does away with the multiplicity of thermal operations, and especially the difficult operation of preliminary dehydration.

To understand better this advantage we have diagrammed in two tables, the order of the operations to be performed at the present

time (Fig. 6) in the treatment of crude oils of Pechelbronn (Alsace) and of those to be performed in adopting the Ab-der-Halden process (Fig. 7).

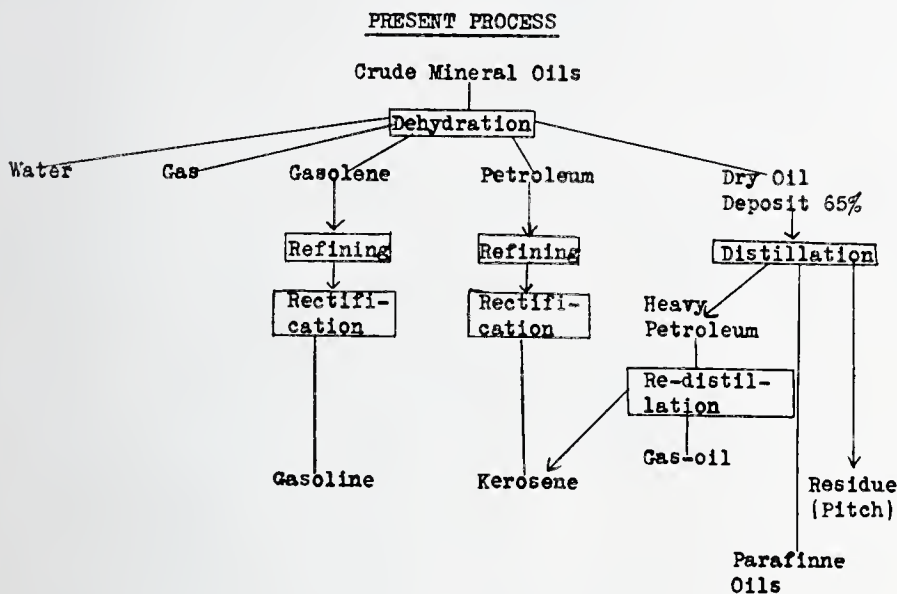


FIG. 6

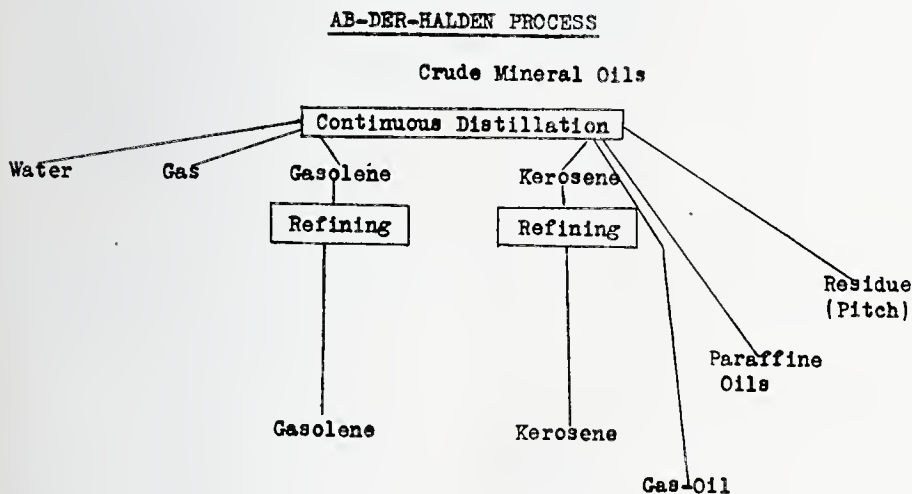


FIG. 7

FIGS. 6 AND 7. FLOW DIAGRAMS FOR THE TREATMENT OF CRUDE MINERAL OILS

When it is a question of crude mineral oil having a low content of asphalt, it is advantageous to separate the operation into two phases.

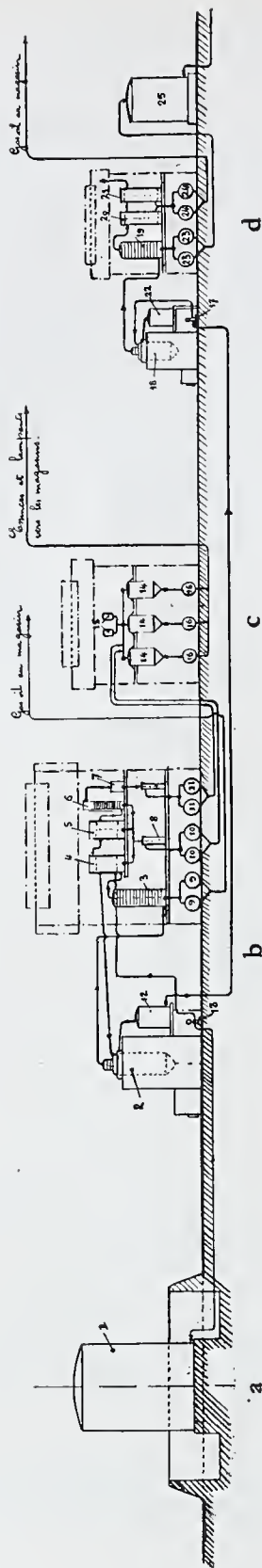


FIG. 8. DIAGRAM OF AN ABDER-HALDEN REFINERY

A. Feeding of raw material: 1, feeding reservoir for crude petroleum, 1000 cu. m.

B. Separation of gasolene, kerosene and gas oil: 2, retort for continuous distillation of raw material; 3, rectifying column for gas-oil; 4, reheater for crude petroleum; 5, kerosene condenser; 6, rectifying column for gasolene; 7, gasolene condenser; 8, water separator; 9, receiving tanks for gas-oil (30 cu. m.); 10, receivers for kerosene (30 cu. m.); 11, receivers for gasolene (30 cu. m.); 12, receivers for residue 65 per cent (30 cu. m.); 13, supply pump of refinery.

C. Chemical treatment: 14, washers; 15, measuring tank for acid; 16, receiving tanks (10 cu. m.); 17, pump for removing hot pitch (residue); 18, retort for continuous distillation of residue; 19, rectifying column for paraffine oils; 20, heat exchanger for steam; 21, water condenser; 22, receiver for asphalt (30 cu. m.); 23, receiver for paraffine oils (30 cu. m.); 24, receiver for gas-oil (30 cu. m.); 25, intermediate paraffine oil tank (100 cu. m.).

In the first phase, the light products such as gasoline or gas oil are extracted and then the residue containing the paraffin fraction and the pitch is treated. This residue which is hot as it leaves the first retort is sent directly into a second apparatus which separates it into paraffine oil and pitch.

The preceding diagram (Fig. 8) indicates the general plan of a refinery established on this principle.

The crude mineral oil coming from stock reservoir (1) is sent through pump (13) by way of pre-heaters (4) and (5) into retort (2).

The mixed vapors (oil and water) issuing from retort (2) after passage through rectification column (3) at the base of which the gas oil is extracted, condense in pre-heaters (4) and (5) giving up their calories to the crude oil, enter into the retort.

Almost all the kerosene is collected at the base of these preheaters and is separated from the condensed water in separator (8).

The gasolene vapors, leaving preheaters (4) and (5) after passage through rectification column (6), separating their last kerosene, are condensed in their turn in condenser (7).

The residue runs in a continuous manner from retort (2) directly through pump (17) into retort (18).

The vapors leaving this retort pass through rectification column (19) at the base of which is extracted paraffine oil.

In condensers (20) and (21) all the vapors are condensed and gas-oil is collected at their bases.

The pitch is eliminated continuously from retort (18) through apparatus (22).

### CONCLUSIONS

The process, whose different industrial applications we have just explained, is based on the known use of steam, but nevertheless presents a new technique.

The carrying over by means of steam of certain fractions of tar or mineral oils is often practiced but we believe that this method, which is applied directly to crude materials, which contain therefore not only all the light and heavy fractions but also water in emulsion, is susceptible of many applications in the treatment of hydrocarbons.

In the process explained the greatest attention is given to the question of thermal recovery which has been pushed to the highest degree. Moreover, the regularity of the speed of the process is assured by considerable thermal control which is represented by the

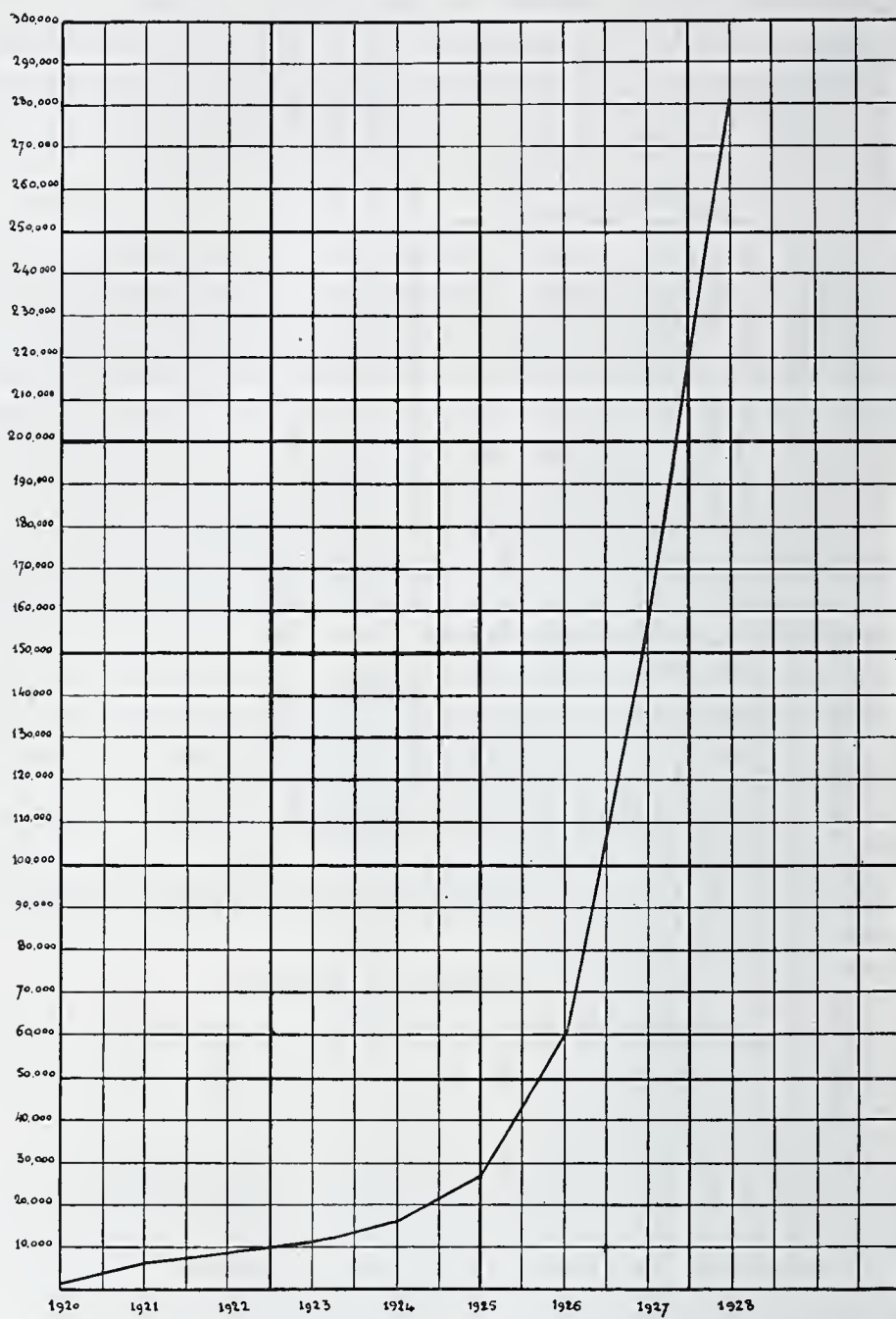


FIG. 9. TAR TREATED ANNUALLY BY THE AB-DER-HALDEN PROCESS

mass of pitch contained in the distillation retort and which facilitates considerably the supervision of the distillation, and reduces the personnel necessary to a minimum.

Finally, this process has the advantage of effecting the continuous distillation of crude materials, without incurring all the inconveniences which are peculiar to this type of operation, but also of obtaining directly a precise selection of various constituents.

It is this last point which constitutes one of the most marked advantages of the Ab-der-Halden process, for it renders possible the direct recovery of products conforming to commercial requirements, without there being need of a redistillation or fractionation.

The development of these applications shown in the graph (Fig. 9) proves the value of this method and the reception which the tar and crude oil industry of Europe has given it.

## CRACKING OF TAR ACIDS FROM COAL

By JACQUES C. MORRELL AND GUSTAV EGLOFF

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In previous work of the authors<sup>1</sup> on the cracking of low-temperature coal tars and tar acids from low-temperature coal tars, it was shown that the high-boiling tar acids were converted principally into tar acids of lower boiling range. The utilization of tar acids from low-temperature coal tar is one of the most important economic phases of low-temperature carbonization. In some cases the tar acids will exceed 40 per cent of the low-temperature coal tars and generally will average 25 per cent. The yield of tar by American practice is approximately 25 gallons per ton of coal. Hence, it is of the greatest importance to find an economic solution of the problem of the disposal of the tar acids.

In the present work the problem is approached from the viewpoint of converting, by the cracking process, the high-boiling tar acids into tar acids or phenols of lower molecular weight and lower boiling-range which possess greater toxicity as antiseptics and have greater utility for other uses, such as wood preservatives, animal dip, phenol aldehyde condensation products, mineral flotation, etc.

Our deposits of coal are the greatest known source of potential energy and by-products. The world reserves of bituminous coal, sub-bituminous coal and lignite are estimated at seven trillion metric tons. The distribution of this enormous quantity of coal is shown in Table I.

The production of coal in 1927 is shown in Table II.

The incentive to commercialize the low-temperature carbonization of coal is the production of a smokeless fuel together with the consideration of decreasing the cost of coal to the consumer while increasing profits to the producer. The elimination of the smoke nuisance in populated areas, particularly large cities, is the chief consideration in the production of a smokeless fuel. The economic success of low-temperature carbonization depends upon the profitable disposal or utilization of low-temperature coal tar and this, in

<sup>1</sup> J. I. E. C. 17, 5, 473, 1925. Amer. Chem. Soc.—Los Angeles, Calif. Meeting, 1925.

turn, depends in a large measure upon the profitable utilization of the tar acids.

Low-temperature carbonization processes are distinguished from those where high temperatures are used in that the former are operated at temperatures from 500° to 600°C., while the latter are operated at temperatures from 1,000° to 1,300°C.

The present low-temperature carbonization processes are characterized by horizontal and vertical retorts of varying form with and without moving elements for keeping the charge in motion, i.e., stationary charge or continuous processes, which may be internally or externally heated.

TABLE I

WORLD RESOURCES OF BITUMINOUS AND SUB-BITUMINOUS COAL AND LIGNITE  
IN MILLIONS OF METRIC TONS

(Reference to table: U. S. Bureau of Mines, 1927.)

	BITUMINOUS COAL	SUB-BITU- MINOUS COAL AND LIGNITE	TOTAL RESOURCES	PER CENT OF WORLD'S SUPPLY
North America:				
United States.....	1,955,521	1,863,452	3,818,973	55.2
Other countries.....	284,162	948,454	1,232,616	17.9
South America.....	31,397		31,397	0.4
Asia.....	760,098	111,851	871,949	12.6
Europe.....	693,162	36,682	729,844	10.6
Africa.....	45,123	1,054	46,177	0.7
Oceania.....	133,481	36,270	169,751	2.6
Total.....	3,902,944	2,997,763	6,900,707	100.0

In general, low-temperature carbonization includes all of those processes where the temperatures are maintained low enough to avoid substantial decomposition of the primary liquid products.

According to Fischer (Fischer-Lessing, *The Conversion of Coal into Oils*, D. Van Nostrand Company, 1925), the tar produced from the distillation of coal with a maximum of 450° to 500°C. does not contain any aromatic compounds such as benzene, toluene, naphthalene or anthracene, the hydrocarbons resembling crude petroleum containing paraffin wax. Further, the primary tars may contain more than 50 per cent of phenols.<sup>2</sup>

<sup>2</sup> Morrell and Egloff J. I. E. C. 17, 5, 473, 1925 analyzed a straight distillate Bé. Gr. 12.8 and reported the following: Tar acids 26.5 per cent; bases 3.25 per cent; unsaturated hydrocarbons 44.25 per cent; aromatic hydrocarbon 9.5 per cent; naphthalenes and paraffins by difference 16.5 per cent.

TABLE II  
PRODUCTION OF COAL IN 1927  
(In metric tons. From U. S. Bureau of Mines, 1928.)

North America:	
Canada:	
Coal.....	12,329,539
Lignite.....	3,465,830
United States:	
Anthracite.....	73,164,000
Bituminous and Lignite.....	471,556,000
Europe:	
Belgium.....	27,573,550
Czechoslovakia:	
Coal.....	14,582,000
Lignite.....	19,769,000
France:	
Coal.....	51,779,300
Lignite.....	1,067,400
Germany:	
Coal.....	153,597,600
Lignite.....	150,805,711
Saar.....	13,595,824
Hungary:	
Coal.....	784,154
Lignite.....	6,243,384
Netherlands:	
Coal.....	9,225,000
Poland:	
Coal.....	37,980,000
Lignite.....	77,000
Russia:	
Coal—Lignite.....	31,000,000
Spain:	
Coal.....	6,023,000
Lignite.....	412,000
United Kingdom: Great Britain.....	259,516,600
Asia:	
India, British.....	21,000,000
Africa:	
Rhodesia, Southern.....	908,744
Union of South Africa.....	12,500,000
Australia:	
New South Wales.....	10,700,000
Total.....	1,475,000,000*

\* Estimates from a number of countries not listed are included in the total.

Morgan and Soule (*Chem. Met. Eng.*, 26, 927 (1922)) show the composition of the low-temperature phenols given in Table III.

Morgan and Soule (*Chem. Met. Eng.*, 26, 1025-30 (1922)) postulate that in the initial decomposition of primary low-temperature coal tar during the carbonization of the coal, the phenols lose side chains by hydrogenation with the formation of lower boiling phenols. Fur-

TABLE III  
COMPOSITION OF THE LOW-TEMPERATURE PHENOLS

COMPONENT	PERCENTAGES BY WEIGHT		
	Phenols	Basis of distillate	Crude tar
Phenol.....	4.2	1.9	0.6
Cresols*.....	33.4	15.2	4.9
Xylenol fraction.....	19.0	8.7	2.8
Higher homologs.....	34.8	15.9	5.1
Pitch (acid resins).....	8.6	3.9	1.3
Totals.....	100.0	45.6	14.7

\* Ratio: 27 per cent ortho-, 19 per cent meta-, and 54 per cent para-cresols.

TABLE IV

	PERCENTAGES BY WEIGHT	
	(1)	(2)
Resin acids (rhetinols).....	10.9	15.5
Phenol.....	0.2	0.7
o-Cresol.....	2.3	} 6.8
m-Cresol.....	2.9	
Xylenols.....	4.7	6.1
Higher phenols.....	8.7	4.7

ther, that the phenols are hydrogenated to aromatic hydrocarbons with the formation of water and further that by hydrogenation with the formation of methane and ethylene. The phenols of low-temperature tar are the principal source of the monocyclic aromatic hydrocarbons.

In an earlier paper (*Chem. Met. Eng.*, 26, 923-8, 977-81 (1922)) Morgan and Soule state that the higher homologs are naphthol derivatives, but contain no naphthol. In general, coals of highest volatile matter yield the most phenols.

F. S. Sinnatt (*Fuel*, 7, No. 7, p. 313) gives the results shown in Table IV on the phenolic substances present in the phenols of low-temperature coal tar, column (1) being taken from the work of Britain, Rowe and Sinnatt (*Fuel*, 1925, 4, 263, et seq.) and column (2) from Parrish and Rowe (*J. S. C. I.*, 1926, 45, 99T).

Gluud and Breuer (*Ges Abhandl. Zur Kennt. der Kohle*, 2, 236–56 (1918)) state that in some cases the phenols will amount to 50 per cent of the low-temperature tar. They showed that partially methylated polyhydroxyphenols and ordinary phenol were absent and stated that the phenol was not a product of low-temperature distillation. All three cresols were identified. In the fractions 220° to 245°C. by acetylation and crystallization of the phenoxyatic acids, it was possible to identify the xlenol and trimethylphenols. The cresols predominate in the fraction 196° to 201°C., but in the higher fractions the xlenols which form almost the whole of fraction 215° to 220°C. are found. Of the cresols, the m-compound is present in the greatest proportion. The yield of cresols seems to be just about double that obtained in gasworks carbonization.

Gluud and Breuer also showed that the cresols are partly destroyed under the conditions of gas making, which was confirmed by passing m-cresol over coke heated to 900°C. The condensed liquid from this experiment contained about one-half phenols and the rest hydrocarbons, mainly benzene. The phenols obtained were insoluble in ammonia and ordinary phenol and o- and p-cresols could not be identified. They concluded that the presence of higher phenols rather than the cresol content of low-temperature tar account for the formation of carboic acid in gas tar.

Weindel (*Brennstoff-Chemie* 3, 245–9 (1922), (Cf. *C.A.*, 14, 1432), (*C. A.*, 17, 1708 (1923)) examined the tar acids from low-temperature tar produced in the Dellwik-Fleischer "Trigas" process. The tar acids were separated and fractionated within close limits. The carbon and hydrogen contents of these fractions were compared with the figures for known phenols. The low hydrogen content points to the presence of unsaturated and polyhydric phenols. These conclusions were confirmed by determining the molecular weight of the phenol acetic esters. B-naphthol was identified.

Schütz, Buschmann and Wissebach (*Ber.*, 56B, 1967–75 (1923); cf. *C. A.*, 17, 2774) examined the phenols from primary tar. Only phenol itself could be isolated by fractional distillation. A combination of physical and chemical methods were used for every other

individual case up to the 240°C. fraction. Phenol, m-cresol, o- and p-cresols, 1,3,5-, 1,2,4-, 1,3,4-, and 1,4,2-xylenols were isolated in the form of derivatives.

Muller (*J. Prakt. Chem.*, 1898, 58, (13, 14 and 15) 1-50). (*J. S. C. I.* 1035 (1898)) studied the effect of subjecting phenol and cresol to a prolonged red heat with the object of ascertaining whether corresponding results are obtained when phenol is gasified per se or in the presence of the higher hydrocarbons. A gas oil having an initial of 220°C., 50 per cent from 300° to 360°C. and end-point of 380°C., with 4 per cent of residue and loss was treated in a like manner. This author concludes that cresol behaves like phenol, the methyl group being split off as methane, while the oxygen combines with one of the carbon atoms of the ring and is eliminated as carbon dioxide when the pure phenols are treated. The gas oil alone yielded 27 per cent of olefins but only 20 per cent when mixed with phenols or cresol.

The formation of benzene from phenol and gas oil is said by Muller to be due to a secondary reaction. The yield was found to vary between 3 and 6 per cent; cresol, however, gave a minimum yield of 10 per cent. In ascertaining the value of gas oil, the percentage of cresol is an important factor as it dilutes the gas with non-luminous products.

Meyer and Hoffman (*Monatsh.*, 38, 343-58 (1917); *J. Chem. Soc.*, 114, 1, 66-7) find that phenol was strikingly resistant to heat and after prolonged heating yielded only a small quantity of decomposition products, among which were benzene and 4-hydroxydiphenyl. In the thermal decomposition of anisole, the methyl group was removed with the formation of phenol. No trihydroxymethylene was observed.

Franz Schütz (*Brennstoff-Chem.*, 4, 85 (1923)) states that the yield of carboic acid from tar can be increased by thermal decomposition of the fraction boiling at 205°C. The phenols were separated from cresols by boiling the mixture with twice its weight of benzoyl chloride. The cresyl benzoate formed is soluble at 25°C. in alcohol, whereas the phenyl benzoate is only slightly soluble at this temperature.

Fischer and Lessing (*The Conversion of Coal into Oils*, 1925, p. 106) state that the phenols found in primary tars are highly resistant to heat. They are decomposed above red heat only and then into carbon (soot) and hydrogen. For that reason they state that a

Diesel engine cannot be run on phenols unmixed with more easily ignitable substances.

Ramage (U. S. Patent 1,208,833) produced phenols by spraying high boiling tar acids by means of a jet of hydrogen into a chamber containing a nickel catalyst heated to 600° to 650°C. and condensing and collecting the phenols as they distilled from the chamber.

Fischer and Ehrhardt (*Ges. Abhandl. Kennt. Kohle*, 4, 280-92 (1919)) subjected the coal tar fraction boiling below 270°C. to oxidation under pressure in a continuous stream of air at 150°C. and at a 40 atmosphere pressure. No definite results were obtained regarding the oxidation of the phenols. The product was a black, lustrous, pitchy material soluble in benzene. The oxidation product of the hydrocarbons separately treated was clear, and also a reddish-yellow oil which deposited solids when cooled and dried in air like varnish.

In an experiment on the oxidation of the tar fraction up to 270°C., the hydrocarbons were scarcely attacked at 100°C., whereas the phenols were extensively changed into resins and acids. Fischer and Ehrhardt conclude that it seems probable that the oxidation products of low-temperature tar are suitable as paints and varnishes.

In later work (*Ges. Abhandl. Kennt. Kohle*, 1919, 4, 237-263; from *Chem. Zentr.*, 1921, i, 762-763) they decomposed potassium and sodium phenolates at 450° to 500°C. Gaseous products including hydrogen and a little methane were produced. In the presence of carbon dioxide, sodium phenolate produced hydrogen and carbon monoxide as well as liquid products. In the presence of carbon monoxide, methane, benzene, and small quantities of phenol were produced. Normal calcium phenolate produces principally phenol. Basic calcium phenolate decomposes at 450°C., giving liquid products as well as hydrogen, methane and carbon monoxide. Decomposition in a stream of carbon dioxide gives calcium carbonate and phenol only. Other phenolates such as barium, aluminum, copper and nickel were studied. The sodium p-cresylates were also decomposed, giving corresponding products to the phenolates. The sodium m-cresylate behaves likewise.

Durand (*Compt. Rend.*, 1921, 172, 1504-1506) decomposed sodium phenolate producing hydrogen, sodium hydroxide, and carbon.

Hofmann and Heyn (*Brennstoff-Chem.*, 1921, 2, 147-150) studied the decomposition of dihydroxydiphenyl. At 485° to 490°C., hydrogen with a little methane or ethane was produced. No carbon

dioxide or carbon monoxide were formed. The distillate contained benzene with appreciable quantities of diphenyl oxide.

Kosaka and Oshima (*J. Fuel Soc. Japan*, 6, 3-8 (English Section) (1927)) found that when the phenols and cresol fractions of low-temperature tar were heated at 850°C. in contact with coke, benzene, naphthalene and anthracene were produced. Benzene and toluene were polymerized into naphthalene and anthracene.

### CATALYTIC REDUCTION OF PHENOLS

The work on the catalytic reduction and conversion of phenols is important because of the possibilities of producing commercially hydrocarbons as well as other compounds from the phenols in low-temperature coal tars or those produced by cracking the higher molecular weight tar acids.

Sabatier and Mailhe (*Compt. Rend.*, 1912, 155, 260-262) made a study of the catalytic action of thorium oxide on phenols. From a mixture of phenols a mixed ether was obtained together with some simple ether; and in some cases simple or mixed oxides of the diphenylene oxide type was obtained. Mixtures of phenol with each of the three cresols produced diphenyl ether and the respective phenyl tolyl ethers. Phenol and  $\alpha$ -naphthol yielded phenyl ether and in addition three distinct crystalline compounds, namely phenyl  $\beta$ -naphthyl ether,  $\beta\beta$ -dinaphthylene oxide and phenylene- $\beta$ -naphthylene oxide. p-cresol and  $\alpha$ -naphthol yielded p-tolyl ether, di-p-tolylene oxide, and  $\alpha$ -naphthylene-p-tolylene oxide, p-cresol and  $\beta$ -naphthol yielded similar products.

The results of experiments by Fischer and Schrader (*Brennstoff-Chem.*, 1, 4-6 (1920)); obtained by passing mixtures of hydrogen with phenols and hydrocarbons through heated tubes at 750°C. are summed up below:

	YIELD OF AROMATIC HYDRO-CARBONS, PER CENT	
	Tinned tube	Iron tube
Three mixed cresols.....	64	5
O-cresol.....	72	35
1,3,4-xyleneol.....	72	5
Hexane.....	7	4
Solvent naphtha I.....	61	63
Solvent naphtha II.....	49	48

With porcelain tubes the yield was negligible. A considerable yield of benzene was produced by the use of an iron tube and tinned iron tubes were found to give the best results, because no carbon separated. Comparison is made between the effect on phenols and hydrocarbons. They suggest that the process may be used to reduce the phenols of low-temperature tars to aromatic hydrocarbons.

Fischer and Schrader (*Ges. Abhandl. Kennt. Kohle*, 6, 128-44 (1921)) made further similar experiments to those described. Phenols were passed through a tinned iron tube. The evolved gases were passed through activated charcoal to remove any benzene present. Technically pure m-cresol heated at 720° to 730°C. with from three and one-half to eight times the amount of hydrogen gave 95 to 98 per cent of the theoretical yield of benzene. For the use of smaller amounts of hydrogen the yield fell off. Lignite creosote gave 58 per cent of its weight of benzene at 750° to 775°C., as against 23 per cent at 720° to 730°C. A low-temperature coal tar fraction, boiling between 200° and 250°C., containing 52 per cent of phenols, produced 44 per cent of its weight of benzene at 750°C. A 200° to 250°C. fraction produced 65 per cent by weight of benzene. Naphthalene was also isolated, indicating the presence of naphthols in the higher low-temperature tar phenol fractions. Experiments were made with reducing agents such as carbon monoxide to avoid the splitting off of methyl groups. Under these conditions m-cresol gave no toluene, but 45 per cent of the theoretical amount of benzene, with a small separation of carbon. Carbon monoxide and water vapor gave no different results, the reaction between carbon monoxide and water taking place very slowly in the tinned iron tube. A mixture of hydrogen and methane did not prevent the splitting off of the methyl group. With hydrogen and water vapor benzene was chiefly obtained, but no phenol was produced. With aluminum-lined tubes the yield of benzene fell off under continuous passage owing to the formation of aluminum oxide. With nickel tubes there was a considerable formation of carbon in the form of soot. By increasing the tinned surface of the tube by placing within it tinned iron filings, the rate of transformation of cresol into benzene could be increased. In later work (*Brennstoff-Chem.*, 3, 289-92 (1922)) a large scale apparatus was used, the tube being 3 m. long and 28 cm. diameter. The capacity of the plant was about 12 kgm. of phenol per hour.

Fischer, Schrader and Zerbe (*Ges. Abhandl. Kennt. Kohle*, 6, 145-53 (1921)) heated low-temperature tar fractions boiling between

200° to 250°C. and 250° to 300°C. at 500°, 600°, 700°, and 750°C. respectively, in a tinned iron tube. Corresponding phenol and hydrocarbon fractions were similarly treated. The most suitable temperature appears to be 600°C. At 500°C. the gasification was only slight, while at 700° and 750°C. separation of carbon was observed. The phenols and hydrocarbons were decomposed in approximately equal amounts. The hydrocarbons yielded far more gas than the phenols. The gas from the tar fractions contained twice as much saturated hydrocarbons as that from the hydrocarbons, and five to eight times as much as that from the phenols. Hence the decomposition of the tar does not follow the same course as that of its components heated separately. Considerable naphthalene was present at the higher temperatures and more naphthalene was obtained from the hydrocarbons than from the phenols.

Fischer and Zerbe (*Brennstoff-Chem.*, 4, 309-12 (1923)) carried on experiments to determine whether iron sulfide could be used to replace tin as an iron covering of the iron tube for the reduction of phenols. The iron tube was coated with iron sulfide by passing  $H_2S$  through it. The reduction of tricresol and brown coal creosote was carried out at 750°C. in a current of hydrogen. No deposit of carbon was observed. The yields of benzene were equal to those obtained when tin was used as a surface coating. A small amount of low-boiling aliphatic hydrocarbons was formed in the process.

G. W. Nen (*Par. Francesa*, 580, 539 (1924); *Anales Soc. Espan. Fis. Quim.*, 24, 77 (1926)) converted the phenols from low-temperature tars into hydrocarbons by distilling in the presence of metallic zinc and aluminum, reduced iron and zinc, or zinc and tin. Up to 150°C. the distillation products do not contain phenols. Above this temperature the vapors are passed through an iron tube containing iron turnings and zinc powder, aluminum or tin. The vapors which then condense do not contain more than 1 to 2 per cent phenols.

#### EXPERIMENTAL CRACKING OF TAR ACIDS

In the present work, tar acids derived from the low-temperature carbonization of bituminous coal were used. Some of the tar acids were received direct, and for some of the experiments they were made by extraction with sodium hydroxide of a straight distillate from low-temperature coal tar, and the tar acids were liberated by dilute sulphuric acid. The straight distillate contained 26 per cent of tar acids. All of the material used was one hundred per cent soluble in

sodium hydroxide and showed the distillation characteristics given in Table V. The neutral oils were not removed from the extract.

In view of the value of the tar acids boiling below 446°F., it was considered desirable to recover this fraction and subject the residue boiling above 446°F. to the cracking process. This residue boiling above 446°F. contains the high molecular weight tar acids which it is desirable to convert into the low molecular weight, low-boiling tar acids of greater economic value.

TABLE V  
SPECIFIC GRAVITY 1.073

FRACTION BOILING FROM:	TAR ACIDS, PER CENT IN EACH FRACTION	PER CENT OF TAR ACIDS	PER CENT ACTUAL TAR ACIDS
245° to 374°F.....		1.2	
374° to 446°F.....	97.2	61.8	60.2
446°F. to end.....	94.8	32.5	30.8
Water.....		3.5	

TABLE VI

Specific gravity.....	1.122
Tar acids.....	94.8 per cent
Initial boiling point.....	430°F.

DISTILLATION ANALYSIS (A. S. T. M.)

PER CENT DISTILLED OVER	DEGREES FAHRENHEIT
10	450
20	482
30	516
40	532
50	500
60	550

The original tar acids after distilling the fraction boiling below 446°F., therefrom analyzed as shown in Table VI.

The topped tar acids were subjected to varying conditions of temperature and pressure in order to obtain maximum yields of low-boiling tar acids. The type of cracking operation used was the production of pressure distillate, gas, and coke by the so-called non-residuum method. The average yield of low-boiling tar acids (below 446°F.) from cracking high-boiling tar acids was 23 per cent.

The effect of temperature and pressure upon the yields of low-boiling tar acids based on the high-boiling tar acids are shown in Table VII.

The maximum yields of the valuable low-boiling tar acids were obtained as a result of pressure distillation of 40 and 75 pounds, respectively.

Table VIII gives the analysis of the pressure distillate resulting from the cracking reaction.

TABLE VII

	40 POUNDS PRESSURE	75 POUNDS PRESSURE	135 POUNDS PRESSURE	200 POUNDS PRESSURE
Liquid temperature, °F.....	785	800	815	850
Fraction to 374°F., per cent.....	0.5	1.6	1.3	3.8
374° to 446°F., per cent.....	22.2	21.4	15.7	11.1
446°F. to end, per cent.....	11.7	7.5	4.6	2.9
Neutral oil, per cent cracking stock..	11.1	9.7	17.2	16.9

TABLE VIII  
OPERATING CONDITIONS

	40 POUNDS PRESSURE	75 POUNDS PRESSURE	135 POUNDS PRESSURE	200 POUNDS PRESSURE
Pressure distillate oil:				
Specific gravity.....	1.019	1.008	1.006	1.004
Per cent cracking stock.....	45.5	44.1	38.8	34.7
Tar acids, per cent of pressure distillate.....	73.2	73.8	66.5	55.7
Tar bases, per cent of pressure distillate.....	3.7	3.4	2.9	3.2
Water, per cent cracking stock.....	3.0	4.0	5.6	7.3

The pressure distillates produced under varying cracking conditions were distilled into three fractions. The percentage yields of the fractions with their tar-acid content were determined and the results are shown in Table IX.

*Gas and Coke Formation.* The tar acids under cracking conditions produce high yields of gas and coke. The gas and coke have a high thermal value and make ideal smokeless fuels. The coke may be used for electrode or metallurgical purposes.

The gas and coke are calculated upon a basis of 42 gallons to the barrel of tar acids cracked (see Table X).

In order to obtain an approximate comparison between cracking topped tar acids and the original tar acids containing all the fractions,

TABLE IX  
OPERATING CONDITIONS

FRACTION BOILING	40 POUNDS PRESSURE	75 POUNDS PRESSURE	135 POUNDS PRESSURE	200 POUNDS PRESSURE
To 374°F., per cent of pressure distillate.....	6.0	9.6	11.2	22.0
374° to 446°F., per cent of pressure distillate.....	51.3	54.6	46.3	40.5
446°F. to end, per cent of pressure distillate.....	30.5	26.0	17.8	24.0
Per cent of tar acids in the pressure distillate fractions:				
To 374°F.....	18.0	38.0	32.6	49.2
374° to 446°F.....	95.0	89.1	87.8	79.2
446°F. to end.....	84.2	65.4	66.6	35.0

TABLE X

	40 POUNDS PRESSURE	75 POUNDS PRESSURE	135 POUNDS PRESSURE	200 POUNDS PRESSURE
Gas, cubic feet per barrel.....	843	750	785	1000
Coke, pounds per barrel.....	184	177	193	181

TABLE XI

FRACTION BOILING	TAR ACIDS, PER CENT IN EACH FRACTION	PER CENT OF PRESSURE DISTILLATE	TAR ACIDS, PER CENT OF CRACKING STOCK
To 374°F.....	77.1	16.7	7.8
374° to 446°F.....	100.0	66.2	38.9
446°F. to end.....	74.9	6.7	2.9
Water.....		8.4	

a test was made at 175 pounds pressure. The test indicates that it is more desirable to distill the low-boiling tar acids from the mixture as the yield of low-boiling tar acids under cracking conditions is decreased. As a matter of fact, the percentage yield of low-boiling tar acids dropped materially below that which was present in the original

tar acid cracking stock. A portion of the low-boiling tar acids present in the charging stock were cracked into gas and coke under the conversion temperature and pressure used.

The tar acids were cracked at an average temperature of 770°F., and 175 pounds pressure. The yield of pressure distillate was 58.8 per cent, the gas and coke, 39.5 per cent; and water, 1.7 per cent. The yield of gas was 490 cubic feet, and coke, 90 pounds per barrel.

Table XI shows the analysis of the fractions of the pressure distillate.

The percentage of tar acids boiling below 446°F. in the cracking stock was 60.2 per cent, whereas the yield of the same fraction after pressure distillation was 46.7 per cent.

#### ANALYSIS OF PHENOLS IN CRACKED PRESSURE DISTILLATE

In the removal of the phenols from the pressure distillate, sodium hydroxide solution was used. It was assumed that this fraction consisted entirely of phenols, excepting a small percentage of neutral oils which was removed by benzene extraction and steam distillation. The presence of possible impurities such as carboxylic acids were not investigated. Morgan and Soule showed that these carboxylic acids were present in the phenols extracted from low-temperature coal tar to a negligible extent only.

Resin acids, or the so-called rhotinols, described by Edwards (*J. S. C. I.*, 1924, 43, 143), if present would be in the fraction boiling above 446°F., which was the maximum temperature at which the high-boiling fractions were cut.

A summary of the boiling points of the lower boiling mono-phenols is given below:

<i>Substance</i>	<i>Boiling point</i>	
	<i>°F.</i>	<i>°C.</i>
Phenol.....	374	190
o-Cresol.....	376	191
m-Cresol.....	397	203
p-Cresol.....	396	202
Xylenols.....	408-432	209-222
Ethyl Phenols.....	397-427	203-219.5
Guaiacol.....	401	205
Creosol.....	426	219
Carvacrol and Thymol boil above.....	446	230

The pressure distillate produced by the cracking of high molecular weight tar acids boiling above a temperature of 446°F., was extracted

repeatedly with 20 per cent by volume of 20 per cent caustic soda or until the extract showed the presence of no sodium phenolate. The composite extract was then washed with benzene to remove suspended neutral oils. The extract was steam distilled at a temperature of about 160°F., to remove the benzene. The sodium phenolate solution was neutralized with dilute hydrochloric acid to a distinct acidity and the sodium chloride solution separated from the liberated tar acids. This aqueous solution of sodium chloride was extracted with benzene to recover any tar acids that remained suspended in the solution. The combined benzene washings and liberated tar acids were then freed of the benzene by the above method and the tar acids dried and weighed.

#### SEPARATION OF MONO-PHENOLS FROM POLYHYDROXYPHENOLS

The methylated derivatives of the polyhydroxyphenols such as creosol and guaiacol were separated from the rest of the phenols by the method of Behal and Choay, described on page 347, Vol. III, of Allen's *Commercial Organic Analysis*.

#### DETERMINATION OF PHENOLS, CREOSOLS, ETC.<sup>3</sup>

The method of Weiss and Downs was used to determine phenols, cresols, etc., in the cracked distillate. A Young's 12-pear fractionating column, using an accurate thermometer reading in  $\frac{1}{2}$  degree or less, was used in the distillation operations.

Briefly, the dry tar acids are distilled at the rate of one drop per second up to 210°C. (Distillate A). The first few drops containing water are collected separately; the tar acids are separated and added to distillate (A). This distillate (A) is weighed and mixed with exactly half its weight of orthocresol (melting point 30.4°C. or above). This mixture is refractionated in the same apparatus as above into fraction (B) boiling at 195°C. (383°F.) and fraction (C), boiling at 207°C. (405°F). Each of these fractions is received in a tared flask, which should be immediately stoppered and weighed. Fraction (B) consists essentially of a mixture of phenol and o-cresol, while fraction (C) consists of a mixture of the three cresols.

*Determination of Phenol.* For examination of fraction (B), is carefully dried with fused calcium chloride. If its phenol content is high as indicated by its specific gravity or a rough freezing point

<sup>3</sup> Allen *Commercial Organic Analysis*, p. 292.

determination, its true freezing point is determined directly. However, if the phenol content is low, a sufficient weighed quantity of pure phenol is added to a weighed quantity of the fraction to bring its specific gravity or freezing point within a proper range. The freezing point of the mixture is now carefully determined, using an air-jacketed test tube equipped with a stirrer and an accurately calibrated thermometer. The mixture is stirred in the test tube until crystallization sets in and the temperature after reaching a maximum begins to fall again. This maximum temperature is recorded as the freezing point and corresponds to a phenol content shown in Table XII. The phenol content obtained is calculated back to the dry tar acids.

*Determination of Cresols.* The ortho and para cresols in fraction (C) were determined likewise by the Weiss and Downs method (*loc. cit.*) and other phenols taken by difference.

TABLE XII

Per cent by weight of phenol.	100	95	90	85	80	75	70
Freezing point, °C.....	40.5	37.9	35.2	32.4	29.4	26.5	23.4

The results of the analysis are tabulated in Table XIII.

*The Cracking of Acid Oil.* An acid oil from low-temperature coal tar containing 36 per cent of tar acids was cracked to simultaneously convert the higher-boiling phenols into lower-boiling phenols and the higher-boiling hydrocarbons into lower-boiling hydrocarbons suitable for motor fuels.

The acid oil was derived from the low-temperature carbonization of coal by distilling the tar to a fuel pitch residue.<sup>4</sup>

The properties of the acid oil used during the cracking operation are given in Table XIV.

The fractions shown in Table XV were obtained from the atmospheric distillation of the acid oil. The content of tar acids and bases are shown.

The acid oil was subjected to cracking conditions of approximately 850°F. liquid temperature and a gauge pressure of 200 pounds per square inch. The pressure distillation was so conducted that cracked distillate, coke and gas were produced. The yield of tar acid-free motor fuel was 25.3 per cent of the acid oil cracked.

<sup>4</sup> Approximately 65 per cent of the acid oil can be obtained from low temperature coal tar.

TABLE XIII

## ANALYSIS OF PHENOLS IN CRACKED DISTILLATE FROM TAR ACIDS

Cracking of tar acids directly

Topping of tar acids and cracking of bottoms above 446°F.

Pressure distillate  
(60.3 per cent by weight of original tar acids)Bottoms  
(67.7 per cent by weight of original tar acids)

	BASED ON PRESSURE DISTILLATE CONTAINING 60.24 PER CENT OF TAR ACIDS	BASED ON TAR ACIDS IN PRESSURE DISTILLATE	BASED ON ORIGINAL TAR ACIDS
Per cent phenol.....	2.04	3.39	1.23
Per cent o-cresol.....	25.69	42.64	15.50
Per cent p-cresol.....	1.66	2.75	1.00
Per cent others.....	30.85	51.22	18.60
Per cent neutral oils...	39.76		24.07
	100.00	100.00	60.30

Bottoms above 446°F.  
or charging stock.  
(36.6 per cent by weight  
of original tar acids)

	BASED ON CUT CONTAIN- ING 88.9 PER CENT TAR ACIDS	BASED ON TAR ACIDS IN CUT	BASED ON ORIGINAL TAR ACIDS
Per cent phenol.....	4.60	5.18	3.12
Per cent o-cresol.....	17.55	19.76	11.88
Per cent p-cresol.....	3.12	3.52	2.11
Per cent others.....	63.63	71.54	44.00
Per cent neutral oil....	11.10		6.59
	100.00	100.00	67.70

## Recapitulation

	CRACKING OF TAR ACIDS DIRECTLY	TOPPING AND CRACKING OF TOPPED TAR ACIDS	
		Topping A	Crack- ing of topped tar acids B
Per cent phenols.....	1.23	3.12	0.17
Per cent o-cresol....	15.50	11.88	0.98
Per cent p-cresol....	1.00	2.11	0.08
Per cent others.....	18.60	44.00	3.66
Per cent neutral oil	24.07	6.59	11.31
	60.30	67.70	16.20
			83.90

Pressure distillate  
(44.4 per cent by weight  
of chg. stock)

	BASED ON PRESSURE DISTILLATE CONTAIN- ING 30.11 PER CENT TAR ACIDS	BASED ON TAR ACIDS IN PRESSURE DISTILLATE	BASED ON TOPPED TAR ACIDS OR CHO. STOCK	BASED ON ORIGINAL TAR ACIDS 16.2 PER CENT BY WEIGHT OF TAR ACIDS
Per cent phenols.....	1.01	3.36	0.49	0.17
Per cent o-cresol.....	6.09	20.20	2.70	0.98
Per cent p-cresol.....	0.52	1.73	0.23	0.08
Per cent others.....	22.49	74.71	10.00	3.66
Per cent neutral oil...	69.89		30.98	11.31
	100.00	100.00	44.40	16.20

Bottoms

The pressure distillate produced from the cracking operation analyzed as shown in Table XVI.

The analysis of the pressure distillate when separated into fractions containing the low-boiling point tar acids is shown in Table XVII.

The low-boiling point tar acids are evidently produced from the high-boiling members. However, it may be well that a portion of

TABLE XIV

A. P. I. gravity.....	12.7
Specific gravity.....	0.981
Tar acids, per cent.....	37.1
Tar bases, per cent.....	4.9
Water, per cent.....	0.5

## DISTILLATION ANALYSIS (A. S. T. M.)

Initial boiling point.....245°F.

PER CENT DISTILLED OVER	DEGREES FAHRENHEIT
10	378
20	404
30	423
40	437
50	460
60	493
70	528
80	571
90	642
98.5	720

TABLE XV

FRACTIONS BOILING FROM	TAR ACIDS, PER CENT IN EACH FRACTION	TAR BASES, PER CENT	PER CENT OF ORIGINAL ACID OIL	TAR ACIDS, PER CENT OF ACID OIL
245° to 374°F.....	22.5	0.0	10.0	2.3
374° to 446°F.....	42.0	2.9	33.5	14.1
446° to 720°F.....	34.9	3.8	56.5	19.7

the tar acids boiling below 374°F. may have been derived in part at least from the fraction boiling between 374° and 446°F. (See Table XIX.)

The motor fuel was found by motor test to be equivalent to 60 per cent of benzol in straight run Pennsylvania gasoline. (See Table XX.)

The gas oil bottoms containing 29.6 per cent of neutral oil and 4 per cent of tar acids boiling above 446°F., based on the raw charge

TABLE XVI

A. P. I. gravity.....	17.3
Specific gravity.....	0.951
Tar acids, per cent.....	32.4
Tar bases, per cent.....	2.2
Water, per cent.....	1.0

## DISTILLATION ANALYSIS (HEMPEL COLUMN)

Initial boiling point.....94°F

PER CENT DISTILLED OVER	DEGREES FAHRENHEIT
10	295
20	335
30	366
40	388
50	405
60	408
70	424
80	455
90	582

TABLE XVII

FRACTION BOILING FROM	TAR ACIDS, PER CENT IN EACH FRACTION	PER CENT OF PRESSURE DISTILLATE OIL	TAR ACIDS, PER CENT OF ACID OIL CRACKED
94° to 374°F.....	22.4	31.5	7.4
374° to 446°F.....	45.2	45.0	20.3
446°F. to end.....	27.2	19.3	5.3

TABLE XVIII

COMPARISON OF THE AMOUNT OF TAR ACIDS PRESENT IN THE ACID OIL BEFORE  
AND AFTER TREATMENT BY THE CRACKING PROCESS

FRACTION BOILING	TAR ACIDS PRESENT IN ORIGINAL ACID OIL, PER CENT	TAR ACIDS AFTER CRACKING ACID OIL, PER CENT
To 374°F.....	2.3	6.0
374° to 446°F.....	14.1	12.0
446°F. to end.....	19.7	7.0

when recycled should increase the yield of tar acids boiling below 446°F. and the yield of motor fuel should be increased to 31.3

TABLE XIX

PROPERTIES OF THE MOTOR FUEL PRODUCED BY CRACKING ACID OIL

A. P. I. Gravity.....	37.3
Initial boiling point.....	150°F.

## DISTILLATION ANALYSIS (A. S. T. M.)

PER CENT DISTILLED OVER	DEGREES FAHRENHEIT
10	238
20	280
30	302
40	320
50	336
60	350
70	364
80	380
90	399
End point	435

TABLE XX

## SUMMARY OF CRACKING RESULTS

Liquid temperature.....	850°F.
Pressure, pounds.....	200
Acid oil:	
A. P. I. gravity.....	12.7
Specific gravity.....	0.9813
Pressure distillate oil (tar acid-free)	
Per cent acid oil.....	55.0
A. P. I. gravity.....	17.3
Alkali soluble tar acids (boiling below 446°F.), per cent acid oil....	26.3
Motor fuel (tar acid-free):	
Acid oil.....	25.3
A. P. I. gravity.....	37.3
Initial boiling point.....	150°F.
End boiling point.....	435°F.
Gas oil:	
Per cent acid oil.....	29.6
A. P. I. gravity.....	12.2
Initial boiling point.....	417°F.
End boiling point.....	708°F.
Gas, cubic foot per barrel of acid oil.....	260
Coke, pounds per barrel.....	40

per cent. The coke and gas yields are increased considerably at the expense of the gas oil bottoms. This gas oil can be used as a wood preservative directly.

*Summary of yields based on cracking 100 gallons charge*

Topped tar acids:

Phenols boiling to 446°F.....	23.5 gallons
Phenols boiling above 446°F.....	7.5 gallons
Neutral oil motor fuel blending stock.....	10 gallons
Neutral oil bottoms.....	3 gallons
Coke.....	425 pounds
Gas.....	1,600 cubic feet

Acid oil:

Tar acids boiling to 374°F.....	6.0 gallons
Tar acids boiling to 446°F.....	12.0 gallons
Tar acids boiling above 446°F.....	7 gallons
Motor fuel (60 per cent benzol equivalent)....	25.2 gallons
Gas oil (specific gravity 0.98).....	29.6 gallons
Gas.....	624 cubic feet
Coke.....	95 pounds

Egloff and Morrell (International Bituminous Coal Conference, 1926) produced 50 per cent of high antiknock motor fuel from the cracking of an acid oil from which the tar acids had been extracted.

### THE CRACKING OF TOPPED ACID OIL

The acid oil as derived from low-temperature coal tar, was topped or fractionated in a batch still provided with a dephlegmator so as to separate the portion distilling below the temperature of 446°F. in order to preserve the valuable tar acids present in this fraction.

Table XXI shows the analysis of the topped acid oil which was subjected to cracking conditions.

The topped acid oil was cracked at pressures of 100 and 200 pounds and temperatures of 810° and 845°F., respectively.

The yields of products are shown in Table XXII.

*Motor Fuel from Cracking Topped Acid Oil.* The pressure distillation of the topped acid oil gave tar acid-free motor fuels of high antiknock properties. They are equivalent to 60 per cent of benzol added to a Pennsylvania gasoline according to motor tests. The properties of the motor fuels and their primary yields derived from the one and two hundred pounds pressure distillation are shown in Table XXV.

TABLE XXI

Specific gravity.....	1.001
Tar acids, per cent.....	34.9
Tar bases, per cent.....	3.8

## DISTILLATION ANALYSIS (A. S. T. M.)

Initial boiling point.....	420°F.
----------------------------	--------

PER CENT DISTILLED OVER	DEGREES FAHRENHEIT
10	445
20	465
30	484
40	500
50	520
60	545
70	568
80	598
90	644
99	692

TABLE XXII

Pressure, pounds.....	100	200
Pressure distillate		
Per cent of charge.....	80.6	66.9
A. P. I., °Gr.....	15.1	18.1
Gas, cubic foot per barrel.....	370	485
Coke, pounds per barrel.....	31	73

## PRESSURE DISTILLATE OIL (HEMPEL DISTILLATION ANALYSIS)

Initial boiling point .....	115°F.	96°F.
Tar acids, per cent.....	25.7	26.4
Tar bases, per cent.....	4.6	2.4
Water, per cent.....	1 8	0.4
PER CENT DISTILLED OVER	DEGREES FAHRENHEIT	DEGREES FAHRENHEIT
10	346	248
20	407	350
30	417	387
40	433	407
50	449	419
60	475	434
70	495	455
80	526	481
90	560	530
	96% 595	98% 600

TABLE XXIII  
TAR ACID CONTENT OF FRACTIONS FROM PRESSURE DISTILLATE  
100 pound run

FRACTION BOILING	TAR ACIDS, PER CENT IN EACH FRACTION	PER CENT OF PRESSURE DISSILLATE	TAR ACIDS, PER CENT OF TOPPED ACID OIL CRACKED
To 374°F.....	16.6	12.4	1.6
374° to 446°F.....	36.9	34.7	10.2
446°F. to end.....	21.2	47.1	10.0

TABLE XXIV  
TAR ACID CONTENT OF FRACTIONS FROM PRESSURE DISTILLATE  
200 pound run

FRACTION BOILING	TAR ACIDS, PER CENT IN EACH FRACTION	PER CENT OF PRESSURE DISTILLATE	TAR ACIDS, PER CENT OF TOPPED ACID OIL CRACKED
To 374°F.....	14.8	26.0	2.6
374° to 446°F.....	32.3	40.1	12.9
446°F. to end.....	20.6	31.5	6.5

TABLE XXV

Pressure, pounds.....	100	200
A. P. I. gravity.....	48.9	43.2
Per cent of cracking charge.....	9.2	20.0
Initial boiling point.....	145°F.	127°F.

DISTILLATION ANALYSIS (A. S. T. M.)

PER CENT DISTILLED OVER	DEGREES FAHRENHEIT	DEGREES FAHRENHEIT
10	200	192
20	230	237
30	256	269
40	276	298
50	300	324
60	320	348
70	342	369
80	367	386
90	402	408
End	437	437

TABLE XXVI

Pressure, pounds.....	100	200
A. P. I. gravity.....	13.8	10.0
Per cent of cracking charge.....	50.4	28.9
Initial boiling point.....	390°F.	431°F.

## DISTILLATION ANALYSIS (A. S. T. M.)

PER CENT DISTILLED OVER	DEGREES FAHRENHEIT	DEGREES FAHRENHEIT
10	434	448
20	452	458
30	462	465
40	476	474
50	489	485
60	504	498
70	526	515
80	548	543
90	589	590
	99% 660	97.5% 651

TABLE XXVII

## SUMMARY OF CRACKING RESULTS.

Liquid temperature.....	800°F.	850°F.
Pressure, pounds.....	100	200
Topped acid oil:		
Specific gravity.....	1.001	1.001
Pressure distillate (tar acid-free):		
Topped acid oil, per cent.....	59.9	49.2
A. P. I. gravity.....	18.0	21.0
Alkali soluble tar acids boiling below 446°F.:		
Topped acid oil, per cent.....	14.8	11.2
Motor fuel (tar acid-free):		
Topped acid oil, per cent.....	9.2	20.0
A. P. I. gravity.....	48.9	43.2
Initial boiling point.....	145	127
End boiling point.....	437	437
Gas oil (containing tar acids):		
Topped acid oil, per cent.....	56.2	35.4
A. P. I. gravity.....	13.8	10
Initial boiling point.....	390	431
End boiling point.....	660	651
Gas, cubic feet per barrel of topped acid oil.....	370	485
Coke, pounds per barrel of topped acid oil.....	31	73

*Gas Oil or Pressure-Distillate Bottoms.* In the atmospheric distillation of the pressure distillate oil to recover the low-boiling tar acids and motor fuel, there is a residue left, so-called gas oil or pressure-distillate bottoms. This fraction is suitable for cracking into further yields of valuable products such as motor fuel or for gas making, or it can be marketed directly as a preservative.

Recycling of the gas oil bottoms should increase the yield of tar acids of low-boiling point by about 0.6 per cent and the yield of tar acid-free motor fuel by about 7 per cent when considering the run made at 200 pounds pressure. The coke and gas are likewise increased considerably at the expense of the gas oil bottoms. The ultimate yield of motor fuel should become 27.0 per cent by the recycling operation. The increase in yields for the 100 pound runs are approximately one-half of those obtainable at 200 pounds pressure.

Table XXVI gives the properties of the gas oil derived from the two cracking tests.

#### REFINING OF CRACKED DISTILLATE FROM ACID OIL AND TOPPED ACID OIL

In the refining of cracked distillates from low-temperature coal tar or distillates derived from it, the tar acids are first removed by treatment with strong caustic solution and the bases subsequently removed by dilute sulphuric acid before proceeding with the main acid and caustic treatment for color and odor.

A typical treatment follows:

1. Treat with about 10 per cent by volume of 30° Bé. caustic soda solution, settle, and draw the sludge.
2. Wash well with water (preferably by showering).
3. Treat with 4 pounds of 66° Bé. sulphuric acid diluted to 10 per cent concentration, settle and draw the sludge. Do not wash.
4. Treat with 4 pounds of 66° Bé. sulphuric acid (but not diluted), settle, and draw the sludge. *Do not wash.*
5. Treat with a second portion of 4 pounds of 66° Bé. sulphuric acid, settle, and draw the sludge.
6. Wash well with water (preferably by showering).
7. Neutralize with about 1 per cent by volume of 16° Bé. sodium plumbite solution, settle, and draw the sludge.
8. Distill with all steam at a maximum still temperature of approximately 250°F.
9. Wash the freshly distilled motor fuel with about 1 per cent by volume of 6° to 8° Bé. caustic soda to improve the odor.

This treatment produced in each case a water-white motor fuel that was light-stable, non-corrosive, and doctor-sweet. The sulphur content was negligible.

It is important to remove the tar acids from cracked motor fuels as they reduce the benzol equivalent of the motor fuel and cause knocking in the motor.

### THE EFFECT OF WATER UPON CRACKING TAR ACIDS

The cracking of tar acids produces water as one of the decomposition products. It was thought that the addition of water in varying percentages would inhibit water formation from tar acids

TABLE XXVIII

A. P. I. gravity.....	0.1
Specific gravity.....	1.073
Initial boiling point.....	410°F.
Water, per cent.....	2.0
Coke, per cent by weight.....	15.3

#### DISTILLATION ANALYSIS

PER CENT DISTILLED OVER	DEGREES FAHRENHEIT
10	422
20	435
30	450
40	475
50	502
60	552
70	615
80	650
87	665

while they are being subjected to high temperature and pressure conditions. It was found that percentages up to 26 per cent water concentration had a small effect only in inhibiting water formation. However, it was found that the decomposition of the tar acids to neutral oil increased as a function of the concentration of water in the reaction zone.

A series of four cracking tests were made at a pressure of 175 pounds upon a tar acid oil which had water present to the extent of 2, 10, 18 and 26 per cent. The tar acids were distilled under pressure to produce distillate, gas, and coke.

Table XXVIII gives a distillation analysis of the tar acid oil by the A. S. T. M. method.

The pressure distillate oils recovered from the cracking tests upon the four tar acids containing water, are recorded with their percentage yields and properties (Table XXX).

### GAS FORMATION

The incondensable gas produced from the cracking reaction of the various water content tar acids and water are given in Table XXXI.

TABLE XXIX  
WATER CONTENT OF TAR ACID CRACKING STOCKS

Per cent water.....	2	10	18	26
Cracking Temperature, °F.....	875	895	880	885
Pressure, pounds.....	175	175	175	175
Total water recovered during cracking:				
Per cent water.....	7.5	13.8	24.2	29.8
Per cent water produced from cracking....	5.5	3.8	6.2	3.8
Tar acid decomposition as function of water present:				
Tar acids per cent pressure distillate.....	84.5	71.6	63.2	54.8
Tar acids per cent basis charge.....	41.9	30.6	18.2	13.3
Tar acids per cent basis tar acids in charge...	42.5	34.0	22.5	17.7*
Neutral oil formation from tar acid decomposition:				
Neutral oil per cent pressure distillate.....	15.5	28.4	36.8	45.2
Neutral oil per cent basis charge.....	7.7	12.2	10.6	10.9
Neutral oil per cent basis tar acids in charge..	7.85	13.6	13.1	15.0*

\* Yield corrected for water in charge.

The gas formation is quite high and increases as a function of increasing water content in the cracking stock. It is important to note that the hydrogen content of the gas is relatively high and might well be an economic source for hydrogen. Table XXXII records the components of the cracked gases from the two extremes with regard to water content.

### COKE FORMATION

The coke derived from the cracking reaction is of honeycomb structure. It is useful not alone for fuel but particularly for electrode or metallurgical purposes.

The coke formation from the cracking of tar acids as a function of the water content is shown in Table XXXIII.

#### DISCUSSION OF CRACKING TAR ACIDS IN THE PRESENCE OF WATER

Franz Fischer (*Brennstoff-Chem.*, 4, 225-34 (1923)) heated samples of coal tar containing from 20 to 50 per cent phenols in an autoclave with water at 200° to 300°C. The higher phenols are

TABLE XXX

Water per cent present in cracking stock.....	2	10	18	26
Pressure distillate per cent of charge.....	49.6	42.8	28.8	24.2
Pressure distillate per cent of tar acids in charge.....	50.5	47.5	35.5	32.6*
A. P. I. gravity.....	9.4	10.1	12.9	13.7

#### DISTILLATION ANALYSES (A. S. T. M.)

Initial boiling point, °F.	195	188	182	186
PER CENT DISTILLED OVER	DEGREES FAHRENHEIT	DEGREES FAHRENHEIT	DEGREES FAHRENHEIT	DEGREES FAHRENHEIT
10	222	260	209	231
20	383	369	350	349
30	393	381	369	366
40	398	388	378	378
50	405	396	387	387
60	411	405	394	396
70	423	415	405	406
80	440	434	420	422
90	523	497	455	461
End point	652	656	616	675
Water	8.0%	5.0%	5.0%	3.0%

\* Yield corrected for water in charge.

soluble to a great extent, thus permitting a partial separation of the phenols from the hydrocarbons. The undissolved hydrocarbons left still contained from 10 to 20 per cent of phenols. The latter are the least acid portion of the phenols. The higher the temperature of the water, the greater the solubility of the phenols in it. The solubility of the hydrocarbons also increases with temperature, e.g., at 300°C. the extracted phenols contained 50 per cent of hydro-



The effect of water on the cracking of tar acids may be summarized as follows within the limits investigated.

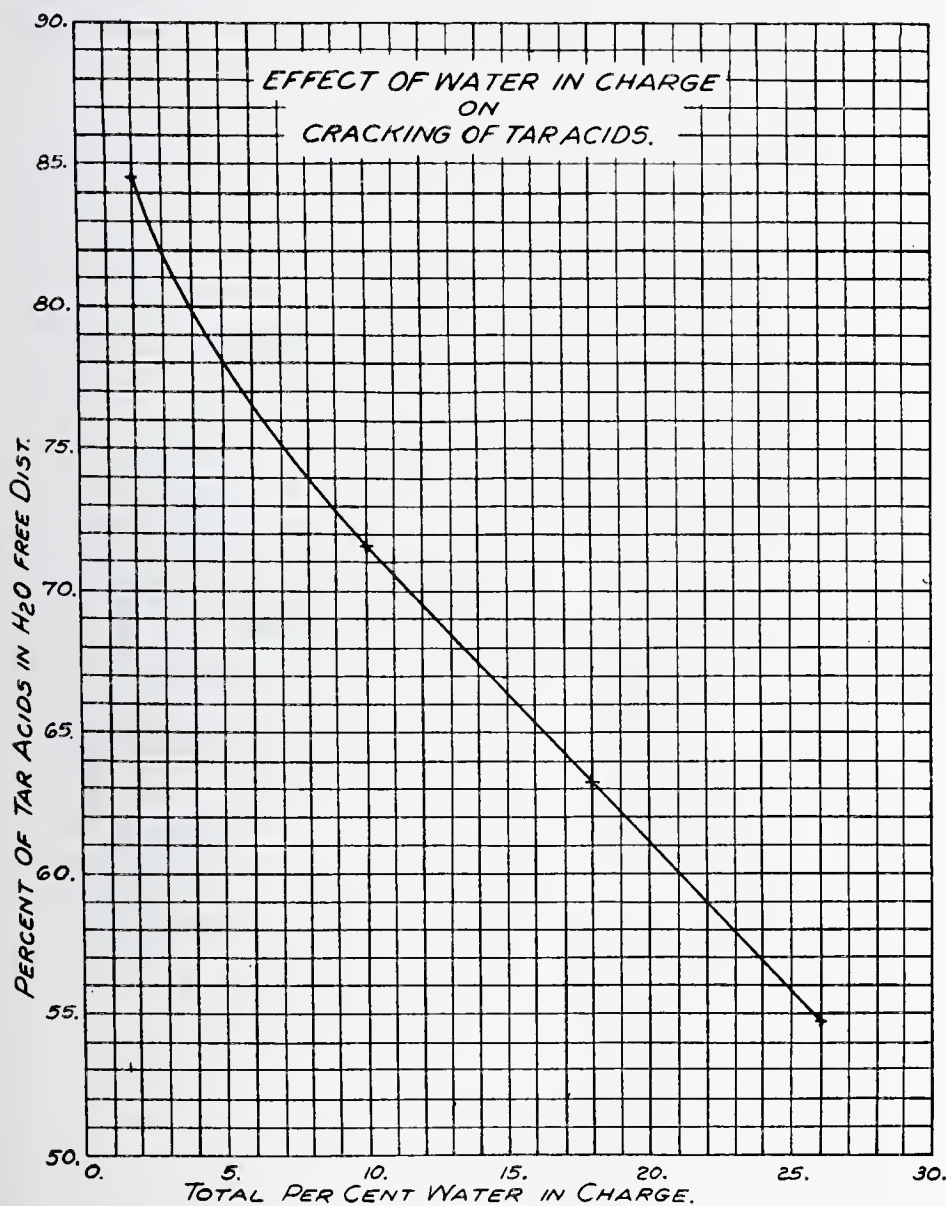


FIG. 1

1. The tar acid content of the pressure distillate decreases proportionately with increase in water content of the charge and the yield based on the tar acids in charge decreases progressively.

2. The neutral oil content of the pressure distillate increases proportionately with increase in water content of the charge.

3. The yield of pressure distillate decreases with increase in water content of the charge, and the specific gravities of the pressure distillate also decrease.

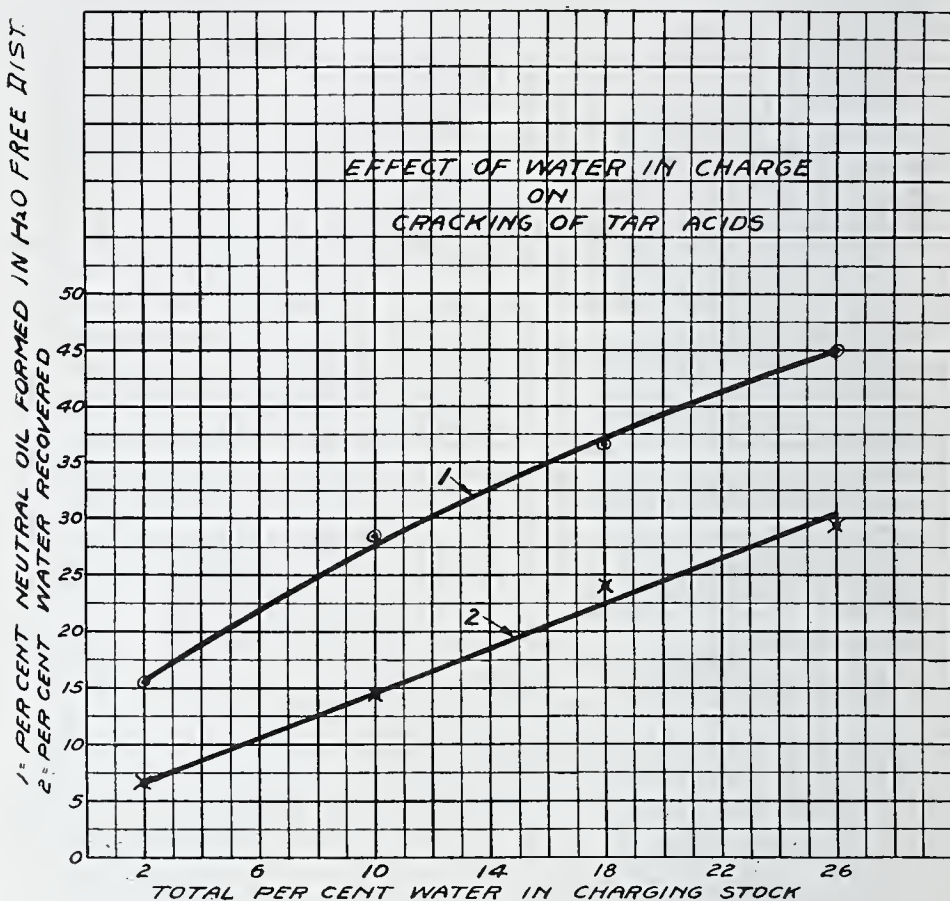


FIG. 2

4. The gas yield is greatly increased with increase in water content of the charge. The coke yield likewise increases but the change is not so marked.

5. The water yield is not greatly affected by the addition of water. The curves (Figs. 1 and 2) show graphically the effect of water in the charge on the formation of tar acids and neutral oils.

## COMMERCIAL PRODUCTS FROM PHENOLS

The principal outlets for phenols at present are as disinfectants, antiseptics, which include animal dips and wood preservatives, and resins from the condensation of phenols and aldehydes. The use of phenols for flotation oils is perhaps a minor application. The catalytic reduction and conversion of phenols to hydrocarbons and other compounds offers future possibilities and further the vast field of valuable derivatives deserves consideration.

## RESINS FROM THE CONDENSATION OF PHENOLS AND ALDEHYDES

The resins made by the condensation of phenols and aldehydes are of the greatest importance in the industries. They are used for making a great variety of things such as artificial amber, buttons, cigar holders, pipe stems, ornamental articles, umbrella handles, grinding wheels, phonograph records, electrical appliances, varnishes, lacquers, enamels, paints, cements, and molding compositions in general.

Bakelite, Redmanol, and Condensite are the three best known phenol-formaldehyde resins. Bakelite, the leading product, is made by condensing phenol with formaldehyde in the presence of a base, e.g., ammonia, ammonium carbonate, sodium or potassium hydroxide or carbonate, amines, etc. The quantity of base should not exceed one-fifth of the amount required to form the phenolate. Where caustic in excess of this is used, sufficient acid is added to neutralize the base down to one-fifth or less of the equivalent amount of phenol used.

The researches into this subject from 1853 to 1900 were general but from 1900 onward they were carried on by many workers with renewed vigor, with the idea of commercial development. Smith (Brit. Patent 16,247, 1889; U. S. Pat. 643,012, February 6, 1900) and Luft (U. S. Pat. 735,278, August 4, 1903) were among the progressive workers of the time in this field who approached very closely the modern principles for the manufacture of phenol resins. However, the later work of Baekeland, Redman and Aylsworth is responsible for the remarkable commercial formaldehyde resins and their adaptation to various uses.

The resins are divided generally into two classes; namely, the soluble and fusible resins and the insoluble and infusible resins. The parent substance is saligenin or the phenol alcohol. By the elimina-

tion of water and condensation, the soluble fusible resins known as the saliretins are formed. By further condensation the insoluble infusible resins, or as Baekeland calls them, resinoids, are formed.

#### USE OF CRESOLS FOR PHENOL FORMALDEHYDE RESINS

Resins have been made from the three cresols, but the o- and p-cresols are generally far less reactive than the m-cresols with formaldehyde and other aldehydes. Generally speaking, the o- and p-cresols are hardened with greater difficulty and are more suitable for making the soluble resins or for use as plasticizing agents. The chief drawback to the use of the o- and p-cresols for making molding resins is the great length of heating required during the hot pressing operation.

#### PHENOLS FROM LOW-TEMPERATURE TAR

Gluud and Breuer (*Ges. Abhandl. z. Kenntnis d. Kohle*, 1919-1920, 4, 230) made a study of the reaction between formaldehyde and phenolic substances obtained from low-temperature coal tar. Soluble, fusible resins were obtained from these phenols by treatment with formaldehyde using ammonium chloride as a catalyst. The presence of hydrocarbons did not appear to interfere with the reaction of resinification. The hydrocarbons could be removed from the resinous products after the reaction was completed. Soluble and fusible brittle resins were also obtained.

Cresols<sup>5</sup> from low-temperature coal tar when treated with benzaldehyde and ammonium chloride formed a thick, brown, viscous material soluble in alcohol and benzol.

When treated to 170°C. under a pressure of 10 atmospheres, a transparent, dark-red, hard resin resulted which, however, was fusible and soluble. With paraldehydes the cresols formed a dark, semi-solid mass of the soluble type. When phenols from low-temperature coal tar and formaldehyde were oxidized in proportions corresponding to one mol. of phenol and one mol. of formaldehyde, using ammonia as a catalyst, a clear resinous product was obtained. By changing the porportion somewhat, a light, yellow, hard, opaque resin was obtained. This product was soluble in alcohol but upon further heating was converted into an insoluble resin. When cresols

<sup>5</sup> Synthetic Resins and Their Plastics, by Ellis—Chemical Catalog Co., Inc., 1923, p. 129.

and xyleneol from low-temperature tar was similarly treated hard, brittle resins were obtained.

Enough has been said on the subject of phenol resins to indicate their importance and the possibility of phenols from low-temperature coal tar to the manufacture of them.

Recent developments in the oxidation of natural gas for the formation of methanol indicate that this process as well as the catalytic processes for making methanol from carbon monoxide and hydrogen are inexpensive and enormous sources of formaldehyde.

It is sufficient to point out here that with phenols from low-temperature coal tar and formaldehyde from natural gas, and carbon monoxide and hydrogen we have an unlimited and cheap source of raw materials for the manufacture of synthetic resins.

#### ANTISEPTICS AND DISINFECTANTS, ETC. DETERMINATION OF PHENOL COEFFICIENTS OF CRACKED PHENOLS

The use of phenol as a disinfectant is so well known that it is our standard of measurement. The crude cresols are also used as disinfectants mainly in solution or dispersion in alkalies, resin soaps, and soaps derived from various oils and fats.

It was thought desirable to determine the phenol coefficients of the following products used or made in the present work.

<i>Material</i>	<i>Phenol Coefficient</i>
1. Tar acids boiling to 374°F. in original before cracking.....	5.7
2. Tar acids boiling 374° to 446°F. in original before cracking...	4.7
3. Tar acids boiling to 374°F. from cracked distillate.....	4.7
4. Tar acids boiling 374° to 446°F. from cracked distillate.....	6.0

The official method described in Bulletin 82 of the Hygienic Laboratory, Public Health Reports was used. By this method the dilution in water found necessary to kill typhoid bacilli was one part of the tar acid fraction to from 470 to 600 parts by weight of water. These values are equivalent to a phenol coefficient of 4.7 to 6.0 as shown, which means 4.7 to 6 times the value of a 5 per cent aqueous solution of phenol. It is believed that higher values could be obtained by emulsifying the phenols as they are only partly soluble in water. The results further show that the cracked phenols are of the same order of efficiency as antiseptics as the phenols of like boiling range in the original tars.

# NEW CATALYTIC PROCESSES FOR THE UTILIZATION OF COAL-TAR CRUDES

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## INTRODUCTORY PART

The purpose of this discussion is to focus attention on some extremely interesting possibilities for the chemical industry arising from the development of new and very effective processes for purifying various crude aromatic hydrocarbons, such as light oil fractions, crude naphthalene, and particularly, crude anthracene by selective catalytic oxidation. This is accomplished by the use of new classes of contact masses which, by selective action, remove part or all of the impurities.

To illustrate the usefulness of such new catalytic processes, I may cite the difficulties involved in the recovery of anthracene of high purity from coal-tar, as hitherto practiced. This has long been one of the most baffling problems in the coal-tar distillation industry. Even yet, the most important source for the technical recovery of anthracene is anthracene oil or green oil. This is the last fraction coming over in the distillation of coal-tar and is collected in the range of temperature of 270° to 400°C. From this fraction 6 to 10 per cent is recoverable as crude anthracene of 15 to 30 per cent anthracene content. The recovery of the crude anthracene from the green oil fraction is made by filtration, centrifuging, and cold and hot pressing. By washing as well as possible with solvent naphtha or creosote oil, the adhering oil and other impurities are to some extent removed and an enriched product is obtained which, however, still contains only some 30 to 50 per cent anthracene.

Many difficulties are encountered in the commercial purification of such grades of crude anthracene to such an extent that the product is sufficiently pure for the production of anthraquinone, which latter is the most important intermediate in the dye-making industry for alizarines and vat colors.

The impurities which must be removed in this purification are many and various. Phenanthrene, acenaphthene, fluorene, carbazol, methyl-anthracene, acridine, etc., are all present, as well as, in many cases, high-boiling paraffins, such as icosane, decosane and

the like. Other impurities are sometimes also present in small amounts and the relative proportions of the different impurities will vary considerably with the nature of the coal-tar from which the crude anthracene is produced. The impurities present in largest quantities, however, are carbazol and phenanthrene. The removal of carbazol, although it is not the most troublesome contaminant, is a critical problem. But the paraffins and the alkyl derivatives of anthracene are not only more troublesome to remove but are also more harmful to the quality of the product.

Many processes have been worked out for the further purification of the various grades of crude anthracene. As examples may be mentioned the removal of contaminants by washing or by recrystallization. Since carbazol in solubility in most solvents and in vapor pressure behaves much like anthracene, special treatments have been devised for its removal, such as conversion to potassium salt by treatment with potassium hydroxide, conversion to nitroso compounds, formaldehyde derivatives and so on. One particular solvent has been found which is somewhat specific for the removal of carbazol and that is pyridine.

All of these processes are expensive and slow. Many require several repetitions in the principal operations and, on that account, are high in labor cost. They entail relatively high health hazards since the crude anthracene contains many compounds which are very irritating to the skin and may even initiate cancerous growths. The processes are also very wasteful since only certain grades of crude anthracene can be used. For example, certain coke oven tars produce a crude having less than 24 per cent, and sometimes as low as 14 to 16 per cent anthracene content. Such crudes cannot be economically worked up by the processes hitherto used. Moreover, cannel coal or other highly paraffinoid coals, when cracked, result in tar fractions containing relatively large amounts of paraffins. These latter contaminants cannot be satisfactorily removed by any of the methods of purification hitherto known so that the raw materials from such tars have been quite useless for making intermediates for dyes.

These considerations are largely responsible for the fact that, in spite of the immense production of coke, and therefore, of coal-tar, in the United States, all efforts to make these domestic sources of anthracene economically available have failed of success. This is a serious handicap to the domestic alizarine and vat dye industries

which are now in a condition of intensive development. The patent literature shows that the failure has not been due to the lack of intensive and well-directed efforts to overcome these difficulties.

As a result of the lack of highly purified anthracene in large enough quantities and at a sufficiently low cost, the anthraquinone used in this country as intermediate for dyes has been made almost exclusively by the synthetic process. This synthesis is accomplished in two steps, namely, the condensation of phthalic anhydride with benzene by means of aluminum chloride and the ring closure of the benzoyl benzoic acid so produced. Although the process is simple at first glance, certain serious difficulties are inherent to it.

Firstly, aluminum chloride of sufficiently high quality is very expensive and difficult to store and handle.

Secondly, in the condensation, hydrochloric acid is produced, involving all the difficult problems due to its great corrosive action, and

Lastly, benzene is used in much more than theoretical quantities involving the usual difficulties and expenses in its recovery ready for re-use.

Altogether, it may be said that while this synthetic process for making anthraquinone has served as a temporary means of overcoming the lack of suitable material for the dye industry, it cannot by any means be called a very satisfactory permanent solution of the problem.

#### CERTAIN NEW PROCESSES

Certain new processes have been devised for purifying various coal-tar crudes and these processes are the subjects dealt with in this discussion. When applied to the purification of crude anthracene, almost any grade can be utilized, even down to 12 to 15 per cent anthracene content. Such low-grade crudes are entirely out of the question for utilization in any of the processes hitherto known. The new processes may be briefly outlined as follows:

Crude anthracene is vaporized and mixed with air which is accomplished preferably by spraying the crude into heated air. The vaporized mixtures are passed over a suitable catalyst which favors total combustion of the heterocyclic impurities and aliphatic compounds. The anthracene is not attacked to any considerable extent. The variety of catalysts which will accomplish this selective oxidation is very large. For, surprising as it may seem, I have found that

carbazol and other nitrogenous compounds, normally considered very stable, are substantially quantitatively burned when subjected in the vapor phase to proper reaction conditions in the presence of suitable catalysts. At the same time, these conditions do not result in any considerable oxidation of the aromatic hydrocarbons present with the heterocyclic compounds and other impurities. The product resulting from such a catalytic purification is a high-grade anthracene containing varying amounts of phenanthrene as almost the only impurity. Even the phenanthrene may be very nearly completely removed by suitable choice of catalyst but it is difficult to remove all of the phenanthrene by catalytic oxidation without seriously reducing the yield in anthracene, since, though phenanthrene is more sensitive to oxidation catalysis than is anthracene, its sensitivity is far less than that of carbazol and the other impurities.

Therefore, most catalysts which reduce the phenanthrene to small amounts will burn up a considerable amount of the anthracene. How much phenanthrene should be removed by catalysis will depend to a large extent on the market for phenanthrene and its derivatives. In solubilities in many well-known solvents, phenanthrene differs very largely from anthracene. It is, therefore, possible by simple and economical recrystallization processes or even by only washing with many solvents to separate the anthracene and phenanthrene practically completely, so that an anthracene of 90 to 99 per cent is easily obtained. Moreover, in the subsequent utilization of the anthracene by oxidation to anthraquinone, the small amount of phenanthrene remaining is necessarily destroyed. In these recrystallization and washing processes, phenanthrene can be recovered in very pure condition from the mother liquors.

It is seen that as a result of this catalytic method of purifying the anthracene, not only is the main product obtained in highly purified condition but by-products, such as phenanthrene, of high potential value can also be obtained in almost any degree of purity which may be required. Since by these processes phenanthrene of high quality is made available at very reasonable costs it is certain that methods for its utilization will be developed along the lines of making new derivatives in the dye and pharmaceutical fields.

As noted above, the paraffin impurities in the crude anthracene are completely removed in these catalytic processes. This attack on the paraffin extends even to alkyl radicals attached to such nuclei as the anthracene grouping. This attack probably proceeds in the stages

that the alkyl radicals are first oxidized to carboxyl groups and the latter lose carbon dioxide, so that the alkyl groups are completely removed. In the old processes for purification of anthracene removal of alkyl derivatives of anthracene was the most difficult problem and was never completely solved. This was particularly unfortunate in that alkyl anthracenes were the most deleterious impurities which could be present in the final product. The overcoming of this difficulty by the catalytic purification processes by choice of suitable conditions for the oxidation and suitable catalysts is one of the most important phases of the improvement accomplished.

#### APPLICATION TO PARTIALLY PURIFIED CRUDES

While the new catalytic purification processes have been discussed as yet only as applied to the crude anthracenes, it is evident that a semi-purified anthracene would serve as excellent material for such processes. There are a large variety of cheap solvents available which will remove the phenanthrene from crude anthracene. The semi-purified product obtained from re-crystallization or washing with such solvents is eminently suitable as a material for the catalytic purification processes since practically the only remaining impurity in large quantities is carbazol, which is completely removed in this catalytic procedure. The product of such a course of treatment is necessarily an anthracene of extremely high purity.

It has been emphasized throughout the discussion that carbazol is destroyed in the course of catalytic purification. It may be desirable at times that the carbazol should be recovered at least in large part. One class of solvents has long been known which will remove carbazol from anthracene. This is pyridine and pyridine-like compounds. In cases where the recovery of the carbazol is desired, a preliminary treatment with pyridine and its derivatives could be used and the semi-purified anthracene obtained could then be subjected to the catalytic purification. The carbazol recovered would carry with it the phenanthrene in large part. But a separation of the two is not only possible by use of known solvents, but by proper choice of catalysts and conditions for the selective catalytic oxidation, the two could be separated so as to leave a highly purified phenanthrene. Later in this discussion, I will call your attention to a new development in the way of solvents which have a selective action in the removal of carbazol and which can be used by the procedure just outlined.

The last two phases of the usefulness of the new catalytic purification processes which have been discussed have dealt with the use of semi-purified anthracene as a material. When such anthracene is used, it is not necessary to stop the oxidation at the stage of producing purified anthracene, and then resume it later to make from the anthracene an anthraquinone by catalytic oxidation. The two stages in the oxidation can be combined either by passing the vapors over two layers of catalyst in the same converter or by taking the vapors of purified anthracene from the first converter and passing it through a catalyst properly selected to its oxidation to anthraquinone in a second converter. In either of these two methods of combining the purification with the oxidation in vapor phase, the first layer of catalyst is properly selected to purify the anthracene and the second layer of catalyst is selected for its oxidation to anthraquinone and by proper choice of the two catalysts, an absolutely chemically pure anthraquinone can be produced in yields of 90 per cent of theory or higher.

As another example of the usefulness of selective catalytic purification, phenolic bodies and other impurities present in crude naphthalene fractions of coal tar can be removed so as to produce a very high grade naphthalene. The latter can then be directly oxidized to such valuable products as alphanaphthaquinone, phthalic anhydride, maleic acid and the like without an intermediate isolation of the naphthalene itself.

Other fractions of coal tar may also be either completely purified or greatly improved by similar treatments. Crude benzol and other crude light oil fractions may be so treated as to remove at least in large part aliphatic, alicyclic, heterocyclic and unsaturated compounds which may be present as impurities.

#### CLASSIFICATION OF CATALYST COMPONENTS

While it is possible to use any suitable oxidation catalyst having a selective oxidizing effect on impurities, I have found that the most effective catalysts are the so-called "stabilized" ones. These are catalysts which contain, in addition to the specific catalytic components, compounds of the alkaline metals, alkaline earth metals and some earth metals characterized by the fact that their oxides are difficultly reducible. These stabilizers exercise a moderating action on the catalyst and prevent or moderate its activity in oxidizing such organic compounds as anthracene, naphthalene, phenanthrene, acenaphthene, benzene, toluene and the like.

Other components, while somewhat active catalytically are not highly specific in their action, may be used in combination with the stabilized catalyst. In such cases these latter components appear to tone or promote the action of the stabilizer present, and in this manner highly efficient selective action of the catalyst is induced. These components are therefore termed "Stabilizer Promoters."

#### COMPLEX COMPOUNDS AS CATALYSTS

The manner in which the catalytically active components are associated with the other components in the mass may effect the action of the mass very considerably. Mixtures of the various elements may be used, but it has also been found that combinations of the elements in the form of base exchange bodies, which may or may not be siliceous base exchange bodies, are also very efficient catalysts for the purposes under discussion.

In many cases it may be possible by variation of the conditions of the catalytic purification to use the same catalyst for different purposes. In other cases the same starting material may be made to yield different main products by varying such conditions as the amount of air or other oxidizing gases, the time of contact, the rate of loading, etc.

The following outlines of experiments serve to illustrate the manner of carrying out the selective catalytic purification processes. The experiments are so chosen as to illustrate the development of catalysts of highly selective activity. In the first experiments relatively simple contact mass compositions are illustrated and in later experiments these are developed to more and more complex structure, at the same time attaining greater selectivity in their action.

#### EXPERIMENT I

Suspend 16 to 18 parts freshly precipitated  $\text{TiO}_2$  in 100 cc. of water which contains 8 to 12 parts of KOH, KCN,  $\text{KNO}_3$  either singly or in admixture. Coat the suspension onto 200 volumes of pumice broken to pea-size.

When 30 per cent crude anthracene is uniformly vaporized with air in a ratio of about 1:25 by weight and passed over the contact mass at  $360^\circ\text{C}$ . a product containing some 65 per cent or more anthracene is obtained. No anthraquinone and 6 per cent or less of carbazol are present in the product. At higher temperatures the products will have about the following compositions:

At 380°C. the anthracene will be 66 or 67 per cent, no anthraquinone and 4 per cent or less carbazol.

At 390°C. 68 per cent or better anthracene, no anthraquinone and less than 3 per cent carbazol. This last product when crystallized from toluene will give a purified product of nearly 95 per cent purity.

At 400°C. the product will contain about the same amount of anthracene, no anthraquinone and the carbazol will drop to 2.5 per cent or less, and finally at 420°C. the product will contain 70 per cent anthracene and slightly above 1 per cent carbazol, no anthraquinone being present.

In all of these products it is understood that phenanthrene makes up the remainder above the sum of the stated percentages.

## EXPERIMENT II

Suspend 16 parts of freshly precipitated ferric oxide in 150 parts of water and dissolve 25 parts of  $\text{KNO}_3$  in the suspension. Impregnate 200 volumes of pea-sized pumice with this suspension and dry it.

The converters suitable for use with such contact mass may be made up of a plurality of tubes of 1 to 3 cm. diameter and surrounded by a cooling bath of high heat conductivity. The bath may consist of mixed potassium and sodium nitrates or nitrites or both, or of molten metal or alloy. In case alloy is used it is very convenient that it should be adjusted in composition to have a boiling point approximately the temperature desired for carrying on the reaction. The mass charged into such a converter may be filled to a layer of 30 to 50 cm. in depth.

Bath converters are not essential to the proper working of this catalyst mass but converters containing provision for automatic cooling by the reaction gases may be used and when so used provision may also be made for the use of heat equalizing mediums of high conductivity through the catalyst. With this catalyst, anthracene containing considerable paraffin, such as that resulting from the tar from distillation of cannel coal or other paraffinoid coal may be purified. Such an anthracene of about 25 to 35 per cent is uniformly vaporized by spraying into a current of hot air, using a ratio of 1 part anthracene to 15 to 40 parts of air by weight. The vapors are led over the contact mass at 360° to 400°C. and the product contains 90 to 95 per cent of the anthracene present in the crude material.

At 360°C. analysis of 70 per cent or better anthracene, no anthraquinone and 6 per cent or less carbazol is obtained on the product.

At 380° the anthracene content rises to nearly 75 per cent, no anthraquinone, and the carbazol content drops to 4 per cent. Such a product can be recrystallized from toluene or solvent naphtha to yield a purified anthracene of 90 per cent or better purity. When the temperature of the purification is raised to 400° to 440°C. a product of 77 to 80 per cent anthracene is obtained while the carbazol drops to 2 per cent or less. After one recrystallization such an anthracene will give a purified anthracene of 94 to 96 per cent purity having only a slight grayish shade.

The materials which have been purified in the manner above specified would have been considered altogether unsuitable for commercial purification by solvent or chemical means as hitherto applied. The products contain none of the oils present in the crude material and the yellowish contaminant, probably chrysogen, is completely removed by the crystallization from coal tar solvent. In addition to the great reduction in carbazol content the phenanthrene content also has been much reduced. The water usually present in such crude materials does not adversely affect the catalytic purification and a drying is simultaneously obtained with the purification since the water is carried away with the waste gases. The product as obtained from the converter shows complete absence of unpleasant odor. The analyses show that the carbazol is substantially completely burned out and the paraffins and liquid lubricating oils containing perhaps phenols and other impurities are also destroyed.

Instead of using the crude anthracene directly, as we have discussed up to this point, it may be given a preliminary purification. Such a semi-purified anthracene containing, say 40 to 60 per cent anthracene content and obtained by one recrystallization from a solvent suitable for phenanthrene removal yields an anthracene of 90 to 96 per cent directly from the converter. This anthracene is suitable for use immediately, either by catalytic oxidation or electrolytic oxidation or chromic acid oxidation. The anthraquinone so obtainable is of excellent purity and can be used without recrystallization or sublimation as a dye intermediate.

The ferric oxide used as the catalytically active component of this mass may be partly or wholly replaced by other metal oxides. For instance, copper oxide made from 55 to 60 parts of crystallized copper nitrate or nickel oxide freshly prepared from 60 to 70 parts of crystallized nickel nitrate, cobalt oxide prepared from 70 to 80 parts of crystallized cobalt nitrate, or 14 parts of cerium oxide, may be used.

The potassium nitrate used in the mass as a stabilizer may also be changed. For example, KOH,  $K_2SO_4$ ,  $KHSO_4$ , KCN,  $K_2CO_3$ , KCl,  $KClO_3$ , KBr, KF, the various potassium phosphates and corresponding compounds of sodium, other alkalies, or alkali earth metals may be used in its place. The stabilizer and the catalytically active element may be introduced into the mass in the form of a complex compound. For instance, potassium ferricyanide will furnish both stabilizer and the catalytically active iron compound. Various silicates in which the catalytically active element may be a silicate or the stabilizer may be a silicate, or both chemically combined, may be used.

When using the copper oxide catalyst, stabilized with KOH or  $KNO_3$ , with a crude of 30 to 35 per cent anthracene content at  $400^\circ$  to  $440^\circ C$ . a product is obtained in which the carbazol is reduced to below 1 per cent and the anthracene content is raised to 70 per cent. Such a product by one recrystallization from solvent naphtha gives anthracene of 95 per cent purity. Sometimes anthraquinone in considerable quantities is formed but the carbazol percentage is never high. Of course, the anthraquinone content is of no deleterious effect and so cannot be considered as an impurity. A yield of 90 per cent of theory or better is obtained.

A nickel oxide-KOH catalyst used with 30 per cent crude anthracene at  $400^\circ$  yields a product containing 74 per cent anthracene, no anthraquinone and less than 2 per cent carbazol.

$CoO-KOH$  and  $CoO-KNO_3$  catalysts are also excellent contact masses. Used with 30 per cent crude anthracene with an air ratio of 1:25 at  $360^\circ C$ . the product obtained contains 72.5 per cent anthracene, no anthraquinone and about 3.5 per cent carbazol.

At  $380^\circ C$ . the anthracene per cent rises to 73.3, no anthraquinone and less than 1 per cent carbazol. This last product by recrystallization gives anthracene of 95 per cent purity. When the catalytic purification is carried out at  $400^\circ C$ . the product contains 75 per cent anthracene, no anthraquinone and practically no carbazol. The phenanthrene remaining as practically the only contaminant of this product can be removed by recrystallization or washing with well-known solvents. The phenanthrene is recoverable from the solvent in a purity of 90 to 95 per cent. Such a contact mass is of a very high degree of effectiveness.

By passing crude anthracene of 30 per cent content through a 40 cm. layer of stabilized cerium oxide catalyst at  $380^\circ$  the product contains 74 per cent anthracene and only 1.4 per cent carbazol.

At a temperature of 400°C. an anthracene of 77 per cent purity is obtained and the carbazol is practically eliminated. Such an anthracene when purified from toluene, using only a minimum amount of the solvent, yields a purified product of 96 to 97 per cent purity, the remainder being phenanthrene. A second recrystallization results in beautifully white anthracene of 99 to 99.8 per cent purity. It goes without saying that phenanthrene of high quality can be recovered from the toluene mother liquors.

### EXPERIMENT III

The quality of the contact mass can be favorably modified by using with the catalytically active component and the stabilizer, a stabilizer promoter. For such stabilizer promoters materials ordinarily considered as dehydrogenating and dehydrating catalysts are very effective. The following is given as an illustration of such a contact mass:

Precipitate 8.7 parts of ferric oxide and 8 parts of  $\text{TiO}_2$  from soluble salts of the two metals by means of alkali. The mixture of the oxides is suspended in 100 parts of water and 14.2 volumes of 10 N KOH are added. The suspension is coated on to 200 to 250 volumes of pea-size pumice in the usual manner and calcined at 400° to 500°C. Using with this mass a crude anthracene of about 30 per cent containing some 22 per cent carbazol, at 380°C. with an air mixture in the ratio of 1:30, a product is obtained in which the carbazol is reduced to about 3.5 per cent. At 400°C. only 1.4 per cent carbazol remains and at temperatures of 420° to 440°C. a Kjeldahl analysis of the product shows no carbazol. The last-named product can be purified from its phenanthrene contaminant in the usual way, resulting in a product of 96 to 97 per cent purity with phenanthrene available as a by-product. In this mass the ferric oxide may be replaced by other metal oxides as also may be the stabilizer promoter,  $\text{TiO}_2$ . It should be noted that with the ferric oxide mass described the phenanthrene is relatively little attacked.

### EXPERIMENT IV

Since the oxides of elements of the fifth and sixth groups, such as  $\text{V}_2\text{O}_5$ ,  $\text{MoO}_3$ , etc. have been described in the literature for use in actual oxidation of the aromatic hydrocarbons catalytically, it might be supposed that such elements could not be used in catalysts intended only for purification. However, by proper selection of stabilizers for ad-

mixtures with such elements they also make very effective catalytic purification contact masses. For instance, prepare a manganese vanadate from 14.4 parts of  $V_2O_5$  dissolved in water containing the proper amount of potassium hydroxide by adding a solution of 14.8 parts of crystallized manganese sulphate in 200 parts of water. The precipitate filtered off is suspended in water containing 10 parts of potassium bromide and sprayed onto 400 volume parts of pumice. The catalyst is used in a converter and under conditions the same as those described above. Using a 25 to 30 per cent crude anthracene, an anthracene of 70 to 80 per cent is produced with the carbazol eliminated as shown by Kjeldahl analysis. The phenanthrene is attacked to a greater or less extent, depending on the operating conditions of the catalytic purification. This product by one recrystallization yields an anthracene of 90 to 95 per cent and with a recovery approximating theory.

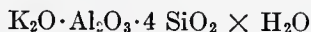
For the manganese vanadate in the mass described above, vanadates of iron, cobalt, nickel, titanium, aluminum, copper and silver, singly or in admixture, may be used. Instead of vanadates, salts of the other metal acids of the fifth and sixth groups may be used alone or admixed with the vanadates. Further, the stabilizer used can be replaced in part or wholly by other halides of the alkali or alkali earth metals. In these substitutions, changes in the amounts of stabilizers and in the conditions of use of the resulting contact masses are mostly desirable.

## EXPERIMENT V

The first four experiments illustrate the making and use of contact masses in which the components are present entirely or largely as mixtures.

In the catalytic purification of coal tar crudes by selective oxidation of the impurities, results, which are even more definitely controllable to the desired ends, are obtainable by combining the components to complex compounds of high molecular weight. For instance, compounds of the nature of zeolites or base exchange bodies not containing silica are eminently adaptable to these purposes.

Let us consider for a moment the formula of a simple zeolite, and using this formula as a starting point show what varied changes can be made in it for use as catalysts for any given purpose.



Since the potassium oxide acts as a stabilizer, the compound is already in part ready for use. However, since this oxide is replaceable to any desired extent by basic oxides, either other stabilizers or stabilizer promoters or even catalytically active oxides can be introduced in this part of the molecule. Further, in making the zeolite the  $\text{Al}_2\text{O}_3$  may also be replaced to any desired degree by other amphoteric oxides and so the nature of the final product can be modified at will by using such oxides as  $\text{TiO}_2$ ,  $\text{Cr}_2\text{O}_3$ ,  $\text{CuO}$ ,  $\text{Co}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$  or other oxides which may serve the purposes of stabilizer promoters and catalytically active components. Lastly, having built a mass which only partly serves the purpose in hand, we have the further flexibility of being able to embed a catalytically active oxide into the zeolite structure. As noted above, non-siliceous base exchange bodies are also available for the uses under discussion. Such compounds are the reaction products of alkali metallates of amphoteric metal oxides with metal salt solutions maintained neutral or faintly alkaline to phenolphthalein, e.g., a solution of potassium aluminate may be treated with solutions of cobalt nitrate or ferric nitrate or with mixtures of these two salts. Such an operation results in a very effective catalyst for the selective oxidation of certain coal tar crudes.

A crude anthracene semi-purified to the extent of the removal of most of the phenanthrene by well-known solvents and then vaporized with air in the ratio of 1:35 and passed over such a catalyst at  $380^\circ$  to  $400^\circ\text{C}$ . produces an anthracene of 96 to 99 per cent purity. The recovery of anthracene is almost theoretical.

## EXPERIMENT VI

To illustrate the use of a double catalytic operation in one converter we may have at the top of the tubes a 30 to 40 cm. layer of an anthracene purification catalyst as discussed in former experiments. Below this catalyst is a 20 to 30 cm. layer of a contact mass adapted to the oxidation of anthracene to anthraquinone. Zeolites containing  $\text{V}_2\text{O}_4$  as one of the amphoteric oxides are eminently adapted for the latter purpose. To make such a catalyst dilute 200 parts of 33° Be. potassium silicate solution with 1,600 volumes of water and add 70 parts of "Celite" earth.

Reduce 18 parts of  $\text{V}_2\text{O}_5$  in water by means of  $\text{SO}_2$  and transform it into the corresponding potassium vanadite.

Mix this latter solution with the silicate suspension, treat this

mixture with so much manganese sulphate solution that it is neutral or slightly alkaline to phenolphthalein. Before use, calcine the mass at 400° to 500°C. with 7 per cent SO<sub>2</sub> gases.

Using a semi-purified anthracene, as detailed in Experiment V, a chemically pure anthraquinone results in yields of 90 to 93 per cent of theory. The purity of this product is such that a freezing point test is the best one to use for detecting minor variations in its quality. Variations of more than 0.1 to 0.2 degree from the freezing point of anthraquinone of the highest purity obtainable show that the operation has not been properly controlled.

### NEW SOLVENT PROCESS

I have frequently pointed out in the discussion up to this point that the carbazol is completely destroyed in the purification processes. The fact that carbazol may become an important material for making dyes, rubber accelerators, etc., led me to a re-consideration of the possibility of the recovery of this value from the crudes.

Liquid compounds containing the furane nucleus were found to possess an extremely high solvent power for carbazol and phenanthrene. On the other hand, the most easily available of these compounds, furfural, was found to dissolve anthracene easily at elevated temperatures and redeposit the solute on cooling. Using this newly discovered property of furfural, recoveries of 94 to 98 per cent of the anthracene from crudes are obtained in the form of greatly purified anthracene. These yields are obtainable either by recrystallization from this solvent or merely by washing processes.

Furfural is relatively cheap and has recently become available in enormous quantities. As compared with the use of pyridine as a solvent for this purpose, we are dealing with a cheaper material and one of relatively pleasant odor, high boiling point and low solubility in water.

By one recrystallization of crude anthracene from furfural we have succeeded in raising the anthracene content from 31 to 86 per cent and at the same time reducing the carbazol content from 16 per cent to approximately 6 per cent. The recovery of anthracene is about 96 per cent, although this may vary by 2 to 3 per cent, depending on the nature of the crude material. Such a product is immediately usable for catalytic oxidation to anthraquinone of highest purity. It goes without saying that the phenanthrene and carbazol are recoverable by known methods from the mother liquor.

By a further crystallization from the same solvent the anthracene purity can be raised to 92 to 96 per cent with only about 2 per cent of carbazol remaining as a contaminant. By using even cheaper solvents which remove phenanthrene and dead oils chiefly, such solvents as orthodichlorobenzene, for example, for an initial purification and following with a treatment with furfural, similar results can be obtained.

The new solvent purification and the new purification by selective catalytic oxidation processes are in a sense rival procedures. By pyramiding the results of either procedure on the other the yields and quality of the product finally obtained leave nothing to be desired in this field of chemical activity.

Such results necessarily could not be obtained without extensive and costly research. The ample research facilities provided by The Selden Company and its policy of encouraging developments of this kind have contributed in no small degree to the successful solution of these problems.

## DISCUSSION

DR. GUSTAV EGLOFF: There really is not much to add to what Dr. Morrell has given you. He has ably presented the primary ideas of this work.

However, it might be well to emphasize a phase of cracking of high boiling tar acids, due to the fact that they have a low economic value, not alone in the United States but in Europe as well and are primarily used for fuel oil. We are building a commercial plant in Belgium at the present time to crack low temperature tars and particularly tar acids.

I made a calculation of the amount of low boiling tar acids of the carboolic acid type, and find on the assumption that the 500-odd million tons of bituminous coal are utilized in the United States, that this quantity of coal if low temperature-treated or even high temperature-treated, could produce for synthetic resin purposes, by the cracking process, something like 5 billion pounds of tar acids of the carboolic type.

Of what practical utility would that be in converting this quantity of cracking stock into phenols? Last year something like 1,700 billion cubic feet of natural gas was consumed in the United States made up approximately of 90 per cent methane gas.

If we had a cheap source of phenols, I am certain that a large quantity of that natural gas would be converted into formaldehyde, so that we could synthesize resins from the phenols of the cracking process and formaldehyde and some ammonia.

I have a dream that condensation products, such as bakelite, should have much wider application than they now have. They are limited due to the high cost, first, of phenols and secondly, formaldehyde, and thirdly, ammonia.

But, when one goes through the streets of any city and sees that deadly

gray color of the buildings for blocks on end, I think it is up to the chemical profession to change the coloring of those buildings by putting a veneer or a surface of a solid plastic, such as bakelite, on there. We can fabricate these bakelite condensation products in color combinations that rival even that color combination that the artist puts on a canvas. We have a cheap method, the cracking process, of converting these high boiling tar acids that are now being utilized for fuel purposes into phenol and formaldehyde. We have an almost inexhaustible source and quantity of natural gas available far beyond any needs for many years to come.

CHAIRMAN PLANK: Does anyone else wish to ask questions or discuss this paper?

R. V. KLEINSCHMIDT (Arthur D. Little, Inc., Cambridge, Mass.): In those experiments with the tin tube what temperature was used?

[DR. MORRELL: About 750°C. As the temperature is reduced the yield falls off.

D. L. JACOBSON (Research Chemist, Koppers Company, Pittsburgh, Pa.): I would like to ask the temperatures you used in the cracking experiments from heavy tar acids to the light tar acids.

Can you give us anything on the composition of the tar acids before cracking?

DR. MORRELL: The temperature was approximately 810°F. The pressures were around 40 to 75 pounds.

As far as the composition of the tar acids, before cracking, is concerned, we accepted the average composition of low temperature tars as given by Soule and Morgan; Sinnatt and others. Of course, we know this definitely—that when you start with tar acids boiling above a temperature of say 446°F., that all of the tar acids boiling below 446°F. are removed. That would mean phenols, cresols, ethyl phenols, etc., are removed and there remains that vague group called retinols or resin acids. I doubt whether the exact composition of these higher phenol boilings are known.

In our work we removed by fractional distillation the phenols which have been isolated in low temperature tar, i.e., the phenols boiling to 446°F. We know the composition, of course, of the low-boiling phenols made by cracking as we made an analysis. Generally, one needs no other basis except boiling range to determine that low boiling phenols are made if the phenols made are determined as a group.

ALFRED T. CHILD (Associate Professor of Chemical Engineering, Rose Polytechnic Institute, Terre Haute, Indiana): In trying to check Dr. Fischer's work in a tin tube, we took the high boiling point phenols and tried to work them the way he suggests, the atmosphere of hydrogen and the temperature he outlines, and we did that with practically negative results. I wanted to know if you had tried that at all?

DR. MORRELL: We did not check Fischer's results. We consider that part of literature, as far as our work is concerned. I assume, of course, that it is all right, as Fischer is a reliable worker.

PROFESSOR CHILD: I wanted to know if it was possible to do that with the tars; i.e., without cracking as you said. I am tremendously interested in what you and Dr. Egloff are doing. If low temperature is going to come into its own it is going to come only as we solve the low temperature tars.

DR. MORRELL: Fischer reported results on phenols and he stated he got mainly benzene. As far as results with the high boiling phenols above 446°, using Fischer's method, I naturally cannot have an opinion. It is subject to experiment only. Of course, we are very much interested in all phases of the subject. If we can reduce the lower boiling phenols, then we can furnish the low boiling phenols by cracking.

PROFESSOR CHILD: If you can get it through one step it would be very interesting.

DR. MORRELL: My own opinion is—and I will form it right here—that I doubt whether he could reduce the high boiling phenols to form hydrocarbons which would be more valuable than the low boiling phenols or hydrocarbons.

PROFESSOR CHILD: Benzene?

DR. MORRELL: He did show that with cresols, toluene is not formed. That is rather interesting. He also tried putting in reducing agents to prevent the splitting off of the methyl group. He formed mainly benzene from cresol. Whether that works on up the line or not, I do not know. According to your experiments it seems Fischer's experiments are not as easily carried out as stated by him.

PROFESSOR CHILD: I understood the Bureau made an attempt to check that without results. We tried aluminum chloride and got rather more encouraging results.

DR. MORRELL: Aluminum chloride with the neutral oils?

PROFESSOR CHILD: Cutting out the phenolic and the tar acids and trying neutral oils, we got decidedly more encouraging results. That was in atmospheric results, not pressure.

DR. MORRELL: I should judge, in passing comment on that, it would be a lot cheaper to crack the neutral oils direct without the aluminum chloride, although the results should be interesting. What was the composition of that distillate? Was that of an aromatic nature?

PROFESSOR CHILD: That was two years ago and I do not remember. We made a distillation of it and I will be glad to send you the fractionation of that.

DR. MORRELL: I would be more interested in the chemical composition, i.e., whether you got one group or the other.

V. E. MEHARG (Bakelite Corporation, Bloomfield, New Jersey): Dr. Egloff mentioned your putting up a plant in Belgium. I could imagine how a plant there might be all right and still not be all right in this country. You mention that this was a commercially attractive proposition. Do you know of any American coal company that is willing to go to the expense of putting up an installation of this type and selling to you their tar with the yields which you mentioned and the processes and cost which you must have, and still believe that they have an attractive proposition in it?

DR. MORRELL: I know a good many who are interested. I might ask this, do you know of a good low temperature carbonization process that is operating at present in this country? One would not consider building a cracking plant for tar before the supply is assured.

We are looking ahead on this thing and I believe that just as special conditions in Belgium can create a profitable, economic condition, so special conditions here can create the same thing. I would not like to make comparisons standing up here on the platform, because there are many conditions affecting prices, but I can show an economic balance considering low temperature coal tar as fuel, and taking the market prices of these various products, provided we can dispose of the quantities that can be made.

That also is a special condition: It may take a dozen, 100-ton a day coal plants, or perhaps a 1,000-ton a day plant to make 500 barrels of oil, and when you take into consideration that a 500-barrel oil tar cracking unit is a small cracking plant, and a 1,000-ton coal plant would be a fairly large one, the thing will not be off balance for some time to come.

The tar is not accumulated very fast and these products have definite value. For example, if we can get formaldehyde cheaply, we will get the resins cheaply enough for wider uses, and I think we can show good economic balances. We are simply trying to do a little pioneer work to point the way and make the whole problem of carbonization a little more attractive.

D. DUNSTAN (Institute of Petroleum Technologists, London): I would like to express briefly my genuine appreciation of the work of Dr. Morrell. For some years past we have been carrying on almost parallel experiments.

I readily confirm the figures that Dr. Morrell brought out. At our end we are not interested in the tar acids. If we were to carbonize all of the raw coal to replace bituminous coal in the household grate, we would have something like 1 billion gallons of low temperature tars which would give us an amount of tar acids that could not be disposed of until Dr. Egloff's dream was realized and one lived in a polychromatic town.

We have been rather concerned in—shall I say—degrading these tar acids into hydrocarbons. Without taking up any more time, I hope tomorrow morning to present a short paper before the Conference dealing with the experimental results to be obtained up to date.

CHAIRMAN PLANK: We are now ready to take up the discussion of Dr. Jaeger's paper on "New Catalytic Processes for the Utilization of Coal Tar Crudes."

DR. ALEXANDER (Carnegie Institute of Technology, Pittsburgh, Pa.): Will the presence of metallic oxide in combination with an acidic oxide, such as calcium vanadate, be as effective in stabilizing as calcium compounds mixed mechanically with the vanadate?

DR. JAEGER: The amount of such kind of stabilizers as alkaline earth must be larger as in chemical combination with the vanadate oxide. The best stabilizers are the alkalis and then the alkaline earth and some of the earth metals. But you can obtain very good results in combining alkalines with alkaline earth.

J. R. M. KLOTZ (Consulting Chemical Engineer, New York, N. Y.): I should like to ask if any known development has been made in this matter? Has the raw material made this way been subsequently converted into dyestuffs?

DR. JAEGER: The anthraquinone so produced is used for making dyes.

MR. KLOTZ: I understood it could be. I wondered if there had been some made.

DR. JAEGER: Yes. Some has been made successfully.

# FUEL PROBLEMS IN THE IRON AND STEEL INDUSTRY

By EDGAR C. EVANS

*National Federation of Iron and Steel Manufacturers, and Honorary Secretary, Institute of Fuel, Westminster, London*

One of the results of the postwar dear fuel period through which most industrial countries have passed, has been an intensive effort towards scientific utilization of fuel in the iron and steel industry.

Fuel economy stations have been established at a number of works and the efforts of these internal organizations have been supplemented by collective organizations established in a number of countries, whose function is to collect and coördinate information regarding fuel consumption at individual works, for the benefit of the industry as a whole.

As the results of these activities, accurate records of practice, frequently under widely varying and extreme conditions, are becoming increasingly available and an attempt can be made to determine from these factors, which are basic in character and which are common to all producing units of the same type, however these may differ in detail.

## STANDARD UNIT OF MEASUREMENT

One of the first essentials in such work is standardization of the units employed. The customary method of expressing fuel consumption in metallurgical processes in pounds of coal per ton of product or by percentage of fuel used is often misleading. It depends upon:

- (1) The calorific value of the fuel used.
- (2) The character of the materials produced and the process.
- (3) The output of the plant in relation to total capacity.

It is preferable therefore to adopt a scientific unit of heat measurement as a basis. Continental works are using to an increasing extent the unit of  $10^6$  calories per unit weight of product or unit area of heating surface.

In Great Britain and the United States the British thermal unit is being adopted as a unit of measurement, but a more convenient unit, probably, in English speaking countries would be the therm (1 therm = 100,000 B.t.u.'s), introduced by the British Fuel Research Board a few years ago. These units— $10^6$  calories or the therm—are used generally in relation to time, area of heating surface or quantity of product.

## CHARACTERISTIC CURVES

Heat consumption per unit of product is to a greater or less extent a function of output. In every heating system operating at constant temperature, a constant amount of fuel must be burnt per unit of time to meet radiation and other external cooling losses. Further, fuel must be consumed proportionately to the amount of material heated so that the total fuel consumption per hour can be expressed by the general equation

$$C = R + xI$$

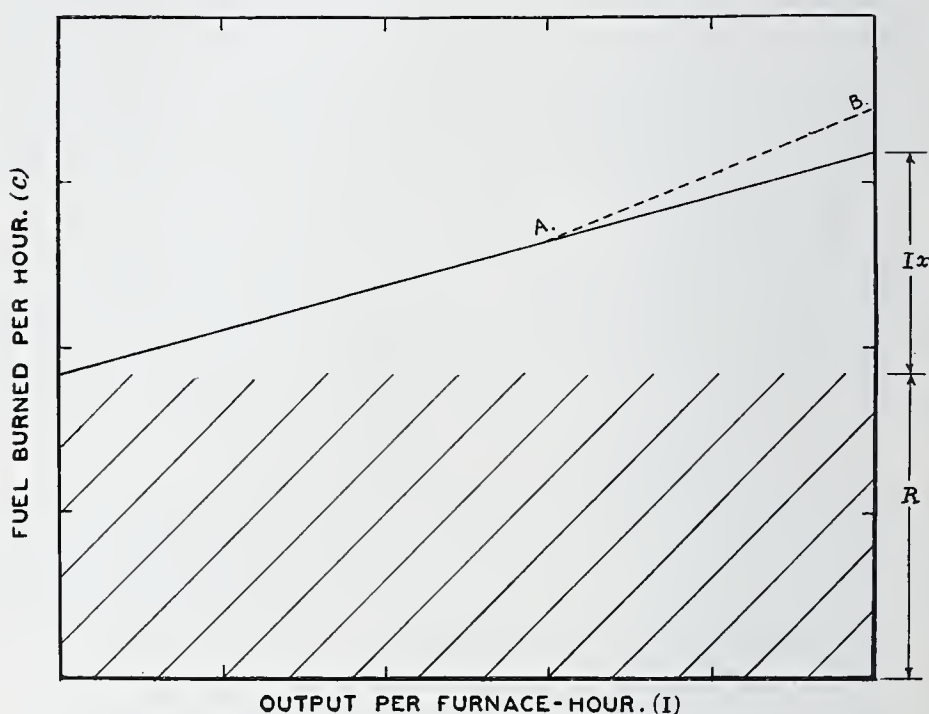


FIG. 1. TYPICAL CURVE OF HEAT CONSUMPTION

Where  $C$  = Pounds of fuel burnt per unit of time

$R$  = a constant representing the pound of fuel per unit of time to make good the external heat losses

$x$  = pounds of fuel per pound of material heated

$I$  = pounds of material heated per hour.

Figure 1 illustrates a typical curve developed on this basis. Curves of this type, have, over a long period, been used as a method of control of boiler firing (the Parsons' line) and are being adopted to an increas-

ing extent in reheating furnace practice. It follows that if radiation and external cooling losses are assumed to be constant irrespective of output, the fuel consumption per unit weight of product will in general fall with increasing output as illustrated in Figure 2. Even in the case of boiler firing and in continuous heating furnaces there is, however, an optimum rate of throughput which if exceeded, necessitates a higher fuel consumption than can be calculated from observations at lower load factors. From fundamental considerations there must be a point at which the rate of passage of the cold material

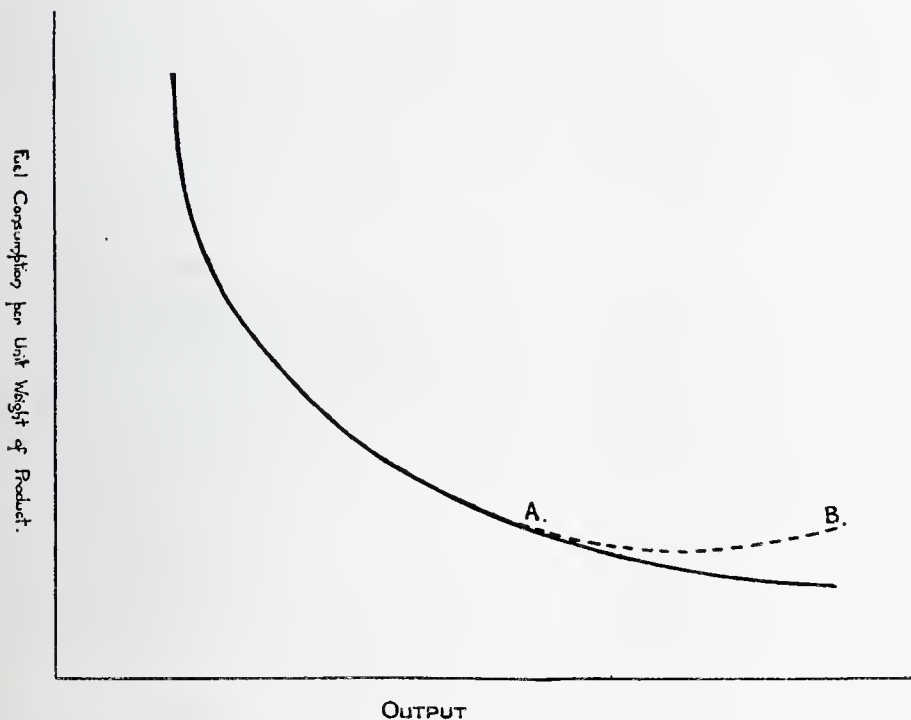


FIG. 2. CURVE OF HEAT CONSUMPTION. RADIATION AND EXTERNAL COOLING LOSSES ASSUMED CONSTANT

through the heating system is greater than that which allows of optimum heat transfer under the heating conditions available, and once the optimum point is passed the fuel consumption per unit of time increases for every further increment in the quantity of material heated. This is represented in Figures 1 and 2 by the dotted portion of the curve AB. The maximum fuel efficiency therefore in metallurgical practice depends upon operation at optimum capacity and the first problem of the fuel engineer is to determine what this optimum capacity is, under conditions at his disposal.

In metallurgical processes as for example reheating practice, where marked interference by chemical phenomena with thermal conditions does not exist, such optimum conditions can be determined by means of characteristic curves in which output and fuel consumption are correlated from results of operation taken over an extended period, making use of curves of the type shown in Figures 1 and 2.

In other metallurgical processes however, where conditions are complicated by chemical reactions, which may be endothermic or exothermic and whose rate in many cases may be altered by the temperature at which they occur, determination of optimum operating conditions by means of characteristic curves may be extremely difficult. On the other hand a study of these processes by means of such curves may throw a light on the chemical phenomena involved and thus assist in finding a solution of problems which would be extremely difficult to define and determine by chemical methods alone.

#### COKE OVEN PRACTICE

For example, in the comparatively simple case of coke oven practice it has been shown recently by K. Rummel<sup>1</sup> that the heat transfer from the walls of the coke oven to the charge during the carbonizing period varies widely at different times during the carbonizing period. Figure 3 gives actual results obtained by the Verein Deutscher Eisenhüttenleute in tests on a battery of silica coke ovens. At the beginning of the carbonizing period heat is absorbed from the oven walls at an extremely rapid rate but towards the latter portion of the period of the charge, heat is being absorbed by the walls from the charge. The following factors are involved:

- (1) The percentage of moisture in the coal.
- (2) The character of the coal and the endothermic or exothermic reactions during the carbonizing period.
- (3) Regularity of heating of the oven walls.

As the result of this work, Rummel states: "It is impossible to assess the efficiency of a coke oven in terms of the heat requirements per kilogram of coke produced, unless the endothermic or exothermic heat for decomposition of the coal under treatment is known. Also the length of the coking period depends on the magnitude of heat of decomposition. With the help of modern measuring devices, the

<sup>1</sup> "Die Wärmeübertragung in den Wänden von Koksöfen." (Paper to World Power Conference, 1928.)

effective heat of coking which is approximately equal to the quantity of heat passing through the oven wall can be calculated from the heat balance. If the effective heat be divided by the total heat supplied, the efficiency of the oven is obtained and its value has to be considered an important index of the proper working of the oven and its control. Furthermore, the consumption of fuel and gas per square meter of heating surface is indicated as providing a useful criterion. The figure expressing the consumption of fuel gas per cubic meter of oven capacity may also be of importance for comparative purposes."

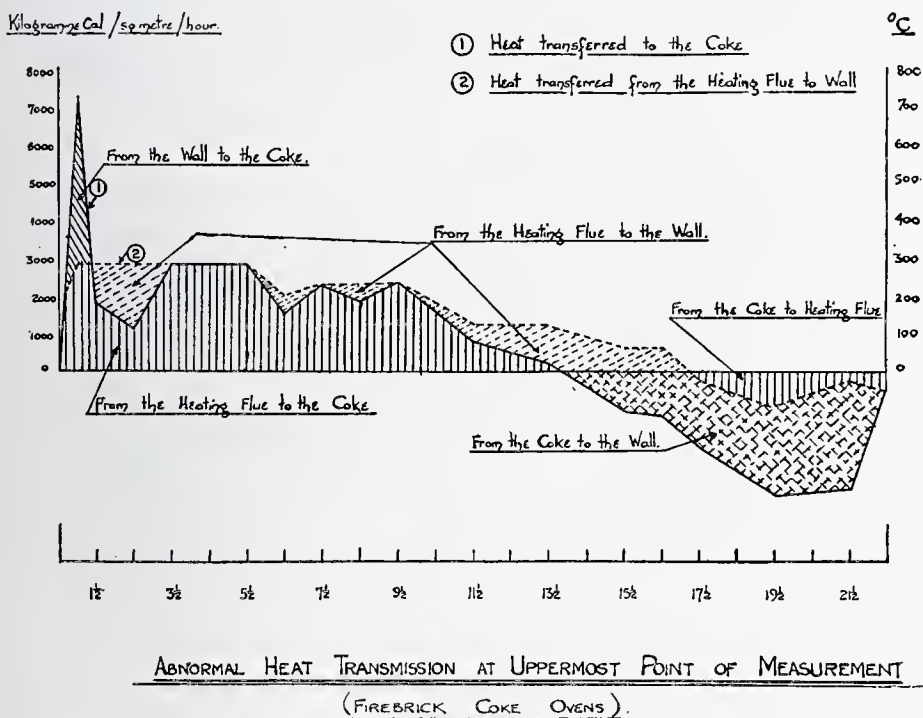


FIG. 3

These observations indicate some of the difficulties of obtaining by thermal methods, even in a comparatively simple process, an adequate measure of the efficiency of heat transfer but they also show how thermal studies can be of assistance in defining the chemical factors involved.

#### BLAST FURNACE PRACTICE

The question becomes still more complex in the case of the blast furnace. Chemical and thermal phenomena are involved which

are interdependent with one another together with factors of operation, of design, of quality of materials used, and so on, which are so complicated in their ultimate effects that their differentiation and evaluation in blast furnace operation are difficult. An attempt however, has been made by Mr. F. J. Bailey and the writer<sup>2</sup> to determine by thermal analysis of blast furnace operating records the principal factors involved.

The method adopted was of a statistical character. Operating results of over 120 furnaces were analyzed to ascertain whether a general "characteristic curve" could be evolved, representative of average blast furnace operation which could, with suitable modifications, be subsequently applied to individual operating practice. To this end the basic equation I.

$$C = R + xI$$

necessarily has to be modified, as the heat supplied in the hearth zone of a blast furnace consists of:

- (1) That produced by complete combustion of carbon to carbon monoxide.
- (2) The sensible heat in the blast.

Further, as the stock heated consists of two products, iron and slag, the heat requirements of which are of a different order and the relative proportions of which vary considerably, it is necessary to subdivide the right-hand side of the equation accordingly. The general formula (1) therefore becomes:

$$C_1 + C_2 = R + XI + YS$$

Where  $C_1$  = pound of carbon gasified at tuyeres per square foot of hearth area per hour

$C_2$  = sensible heat introduced with the blast, reckoned as pounds of carbon (burnt to CO) per square foot hearth area per hour

$R$  = heat requirements per square foot of hearth area per hour to meet external loss

$X$  = the heat requirements per pound of iron made

$I$  = pound of iron made per square foot of hearth area per hour

<sup>2</sup> "Blast Furnace Data and their Correlation." *Jour. Iron and Steel Inst.*, Vol. I, 1928.

Y = heat requirements per pound of slag made

S = pound of slag made per square foot of hearth area per hour

The carbon burnt at the tuyeres can be determined by the formula devised by P. H. Howland.<sup>3</sup>

$$C_1 = \frac{\text{Total carbon gasified} \times \% N_2 \times 40.06}{(\% CO + \% CO_2) \times 75.8}$$

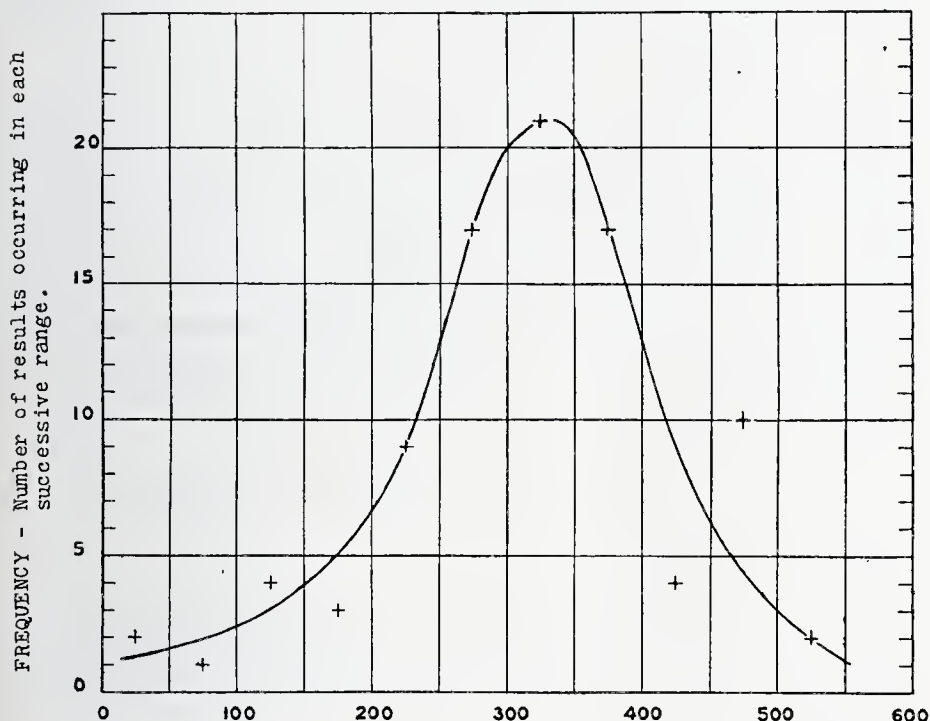


FIG. 4

Where  $C_1$  = carbon gasified at the tuyeres = fixed carbon in coke + carbon in limestone and ore - carbon in pig - carbon in flue dust.

In actual practice, however, difficulties are experienced in obtaining from customary returns, a figure representative of the total carbon gasified, whilst in many cases gas analyses reported were open to suspicion as being hardly representative of average values. A frequency diagram (Fig. 4) was therefore constructed from returns

<sup>3</sup> *Trans. Am. Inst. Min. Eng.*, 1916-17, Vol. LCI, pp. 339-364.

available which could be considered as reasonably reliable and as the number of results giving a figure of about 350 of carbon per ton pig iron used other than at the tuyeres predominated, this figure was adopted as a constant for purposes of a first approximation, the carbon burnt at the tuyeres being therefore assumed to be carbon charged in the coke less 350 pounds. The equivalent expressed in pounds of carbon per square foot hearth area per hour of the sensible heat in the blast could be directly calculated from the carbon burnt at the tuyeres by the formula.

$$C_1 \times 0.000317 \times \text{temperature of blast in degrees Fahrenheit}$$

The heat production side of the equation therefore could be easily calculated, but the heat absorbed was difficult to determine. In order to obtain a value for R, applicable to all furnaces, it was assumed from the results obtained by P. H. Royster and T. L. Joseph of the United States Bureau of Mines, that hearth temperatures of all blast furnaces were approximately equal,<sup>4</sup> from which the heat lost from the hearth by radiation and external cooling losses could be expressed as

$$\frac{K}{D} \text{ pounds carbon per square foot hearth area per hour}$$

Where K = a constant.

D = hearth diameter in feet.

By graphical and statistical methods of the results available, values of K, X and Y were determined and as a first approximation, an actuarial average of the furnaces examined gave mean values for these factors of

$$\begin{aligned} K &= 500 \\ X &= 0.56 \\ Y &= 0.28 \end{aligned}$$

so that the average equation for the furnaces examined became

$$C_1 + C_2 = \frac{500}{D} + 0.561 + 0.28S$$

On applying these average values to results of individual furnaces it was found that some modification of the factor 500 had to be made

<sup>4</sup> "Symposium on Pyrometry" held by the *Amer. Inst. Min. and Met. Eng.*, 1920, pp. 544-558.

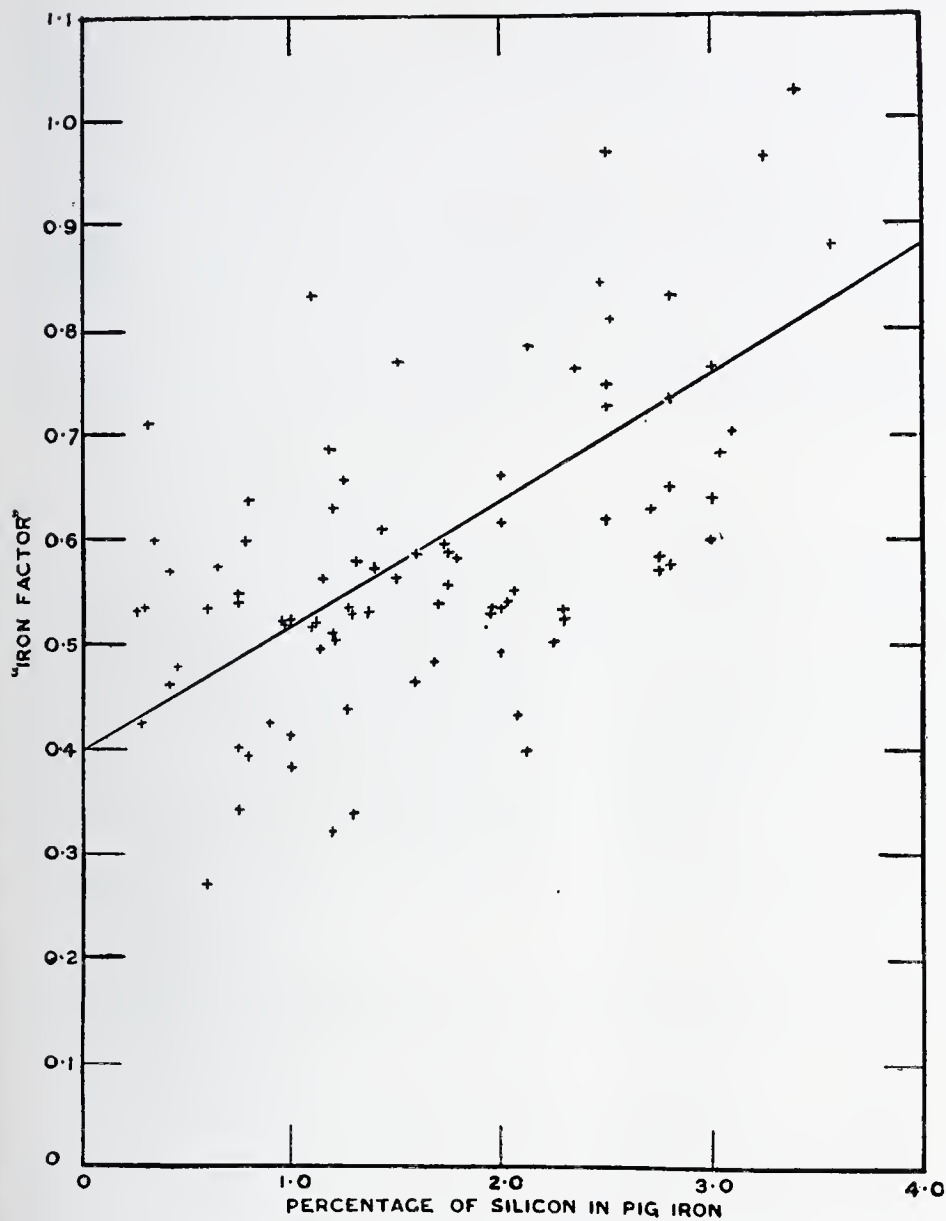


FIG. 5. RELATION BETWEEN PERCENTAGE OF SILICON IN PIG IRON AND THE IRON FACTOR

for furnaces of small hearth diameter, where little or no water cooling was used. In such cases, the value of  $R$  found in using this factor, was too high and results had to be adjusted accordingly.

From information available, variation of the hearth heat require-

ments of different slags are not of a sufficiently large order to affect the calculations at the present stage, and the factor 0.23 has been assumed to be sufficiently constant to be representative under all conditions.

In the case of the iron factor  $X$ , however, correlation of the basic equation with practical results could only be obtained by assuming that this factor differed widely under different conditions. The first variable to be studied was the quality of the iron and it was found that there seemed to be a definite relationship between the percentage of silicon in the pig iron and the iron factor. This relationship is shown in Figure 5 and the average equation was deduced from this curve.

$$X = A + 0.12 \times (\text{percentage silicon})$$

The next variable examined was "time in the furnace." In general the factor  $X$  was a measure to some extent of the heat absorbed in the hearth by so called direct reduction, and this would depend to a great extent upon the efficiency of contact between the reducing gas and ore. In this case, some relationship should be obtainable between the time of the material in the furnace and the factor  $X$ . A graphical study of the results available gave a curve represented by Figure 6 which indicates a definite relationship between the length of time the materials are in the furnace and the iron factor—the longer the material is in the furnace, the lower the iron factor.

It is evident at this stage, that there must be in blast furnace operation an optimum rate of driving dependent not only on physical conditions of heat transfer between the ascending gases and the descending material but also on thermo-chemical considerations depending upon the time and efficiency of contact of the reducing gasses on the descending iron bearing materials.

Thermal analysis therefore allows of a measure not only of the thermal efficiency of the blast furnace but also of its chemical efficiency, the primary condition for which is effective contact between ore and reducing gas.

In this connection A. E. MacCoun in discussion of a paper by T. L. Joseph<sup>5</sup> pointed out that in a furnace of 19 feet 7 inches diameter, making 700 to 725 tons daily "It was found in some instances

<sup>5</sup> Year Book. *Am. Iron and Steel Inst.*, 1927, p. 456.

that the stock came into the region of the tuyeres from the point of entry in the furnace in three hours and forty five minutes. This was hard to believe and it was tested by passing cables down with the stock; and gauging it from the travel of the cables half-way down, it was proven that the time required for part of the stock to travel from the top of the furnace to the tuyeres was 3 hours and 45 minutes. From this it is evident that there must be considerable dead space at some places in the furnace."

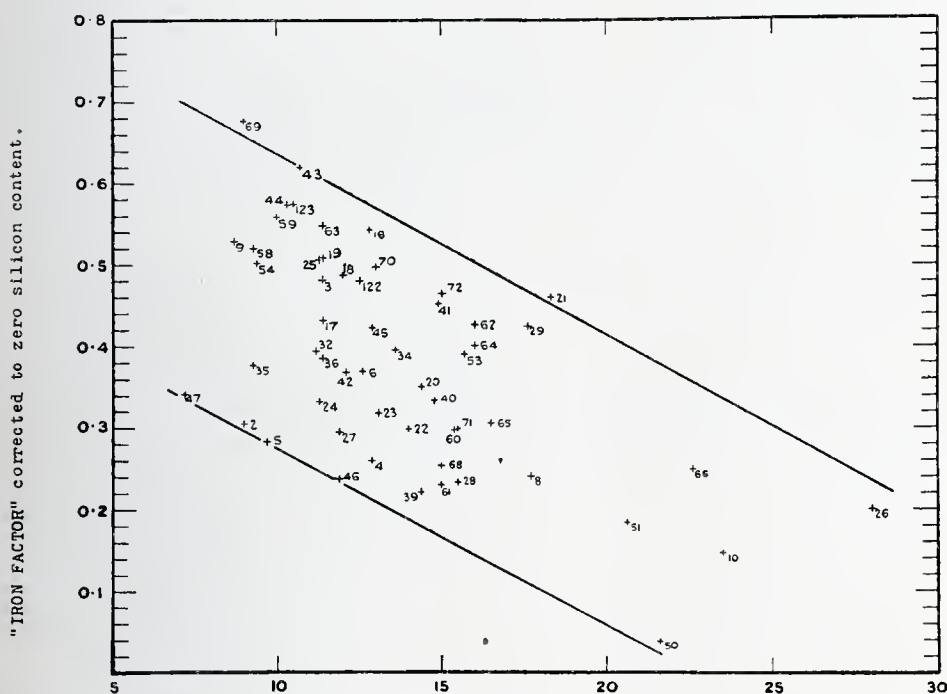


FIG. 6

The result of such conditions would probably be that the X factor would be increased, due to increase in the proportion of so-called direct reduction and consequent higher thermal requirements. Any attempt therefore, to increase the rate of production beyond the optimum (and thus reduce the standing thermal requirements per unit of product to a minimum) will be counter balanced by reduced effective time of contact between reducing gas and ore and it is difficult to reconcile these two opposing factors.

#### REDUCTION OF RADIATION AND EXTERNAL COOLING LOSSES

Radiation and other external cooling losses per unit of hearth area are up to a point, reduced with increasing hearth diameter, and

for that reason, other factors being equal, large hearth diameters should be more economical than small hearths. On the other hand, in view of the work of the United States Bureau of Mines<sup>6</sup> there must be a limit to effective increase of hearth diameter. These authorities have shown that oxygen is removed from the blast within a distance of 40 inches from the nose of the tuyeres, and the larger the hearth the greater the volume in the hearth area where the heat producing reactions cease to exist and where in fact, endothermic reactions probably predominate.

Another expedient that could be adopted would be to reduce the amount of water cooling used in the hearth and bosh areas. This, however, raises the problem of suitable refractories if high rates of production are to be maintained with satisfactory life of the linings so that there appears to be definite limitations to reduction in modern practice of the standing thermal charges of the furnace.

#### IMPROVEMENT IN EFFECTIVE TIME OF CONTACT BETWEEN GAS AND ORE

Possibly the greatest possibilities of improvement in customary blast furnace operation lie in increasing the efficiency of contact between gas and ore. Several difficult problems, however, arise. Firstly, reduction is effected by an upward current of gas which rapidly cools as it passes through the furnace. In accordance with the principles enunciated by Professor Groum-Grjmailo it would be extremely difficult even assuming that the furnace were filled with broken solids, more or less homogeneous in size, to avoid channelling of the gas, but the problem becomes still more complicated by

- (a) the heterogeneous character of the material charged.
- (b) changes in density, composition and structure which occur as the material descends through the furnace.

A study of one factor only, the chemical changes that occur, will illustrate some of the complexities of the problem. It has been shown by W. A. Bone, L. Reeve and H. Saunders<sup>7</sup> that when ore is acted upon by reducing gas between the temperatures of 350 and 550°C. after a certain proportion of iron has been reduced, the obscure reaction of carbon deposition



<sup>6</sup> *Trans. Am. Min. Engs.* C. St. J. Perrott and S. P. Kinney, 1923, pp. 543-586.

<sup>7</sup> *Iron and Steel Inst.*, Vol. I, 1927.

TABLE I

## Furnace lines:

Height.....	72 feet 9 inches
Hearth diameter.....	11 feet 0 inches
Bosh diameter.....	19 feet 10 inches
Bosh height.....	15 feet 6 inches

## Pig iron:

Output per week, tons.....	1450
Character.....	basic
Analysis, per cent:	
Si.....	0.70-1.25
S.....	0.08-0.04
P.....	1.25-1.50
Mn.....	1.75-2.25
C.....	

## Coke:

Cons. per ton pig, pounds.....	2520
Character.....	moderate
Average analysis, per cent:	
Fixed Carbon.....	79.0
Ash.....	10.7
Moisture.....	8.0
Sulphur.....	1.45

## Limestone:

Cons. per ton pig, pounds.....	730
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## Ore:

Cons. per ton pig, cwt.....	45.5
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## Blast:

Temperature °F.....	1100
Pressure, pounds per square inch.....	9½

## Slag:

Prod. per ton pig, pounds.....	2350
Analysis, per cent:	
SiO <sub>2</sub> .....	31.0
CaO.....	42.0
Al <sub>2</sub> O <sub>3</sub> .....	16.0
MgO.....	2.0
S.....	2.5
FeO.....	1.5
MnO.....	

TABLE I—*Continued*

Analysis, per cent:	
CO <sub>2</sub> .....	10.0
CO.....	28.0
H <sub>2</sub> .....	3.0
N <sub>2</sub> .....	59.0
Temperature, °F.....	400
Iron produced per square foot hearth area per hour.....	203.5 pounds
Slag produced per square foot hearth area per hour.....	213.5 pounds
Carbon gasified as tuyeres per square foot hearth area per hour.....	149.0 pounds
Equivalent carbon (including sensible heat in blast) per square foot hearth area per hour.....	201.0 pounds
External loss requirements as pounds of equivalent carbon per square foot hearth area per hour.....	45.4
Slag requirements per square foot hearth area per hour....	59.8
Iron factor (including silicon).....	0.471
Iron factor (excluding silicon).....	0.350

predominates and from practical experience, this is frequently associated with a change in the volume and structure of the ore. Any attempt to solve mathematically the problems of distribution based on the size of the materials as charged, is complicated by chemical phenomena occurring within quite a short distance from the stock line.

The work of the United States Bureau of Mines on this question is of peculiar interest and importance and whilst complete mathematical solution is probably extremely difficult to obtain, results already available help to throw light on the problems we had.

A further difficulty, however, arises from the mechanism of the blast furnace process. Although observations of furnaces which have been blown out afford some indications of the method of passage of solid material downwards, very little appears to be known of the mechanism of the process itself. In this connection some recent results of preliminary observations by a British plant may be of interest. The average operating conditions are given in Table I and in addition the following observations are at present being made:

- (1) Continuous automatic analysis of blast furnace gas.
- (2) Continuous records of pressure and temperature of blast.
- (3) Volume of blast (the latter being measured by a differential pressure meter installed after the stoves).

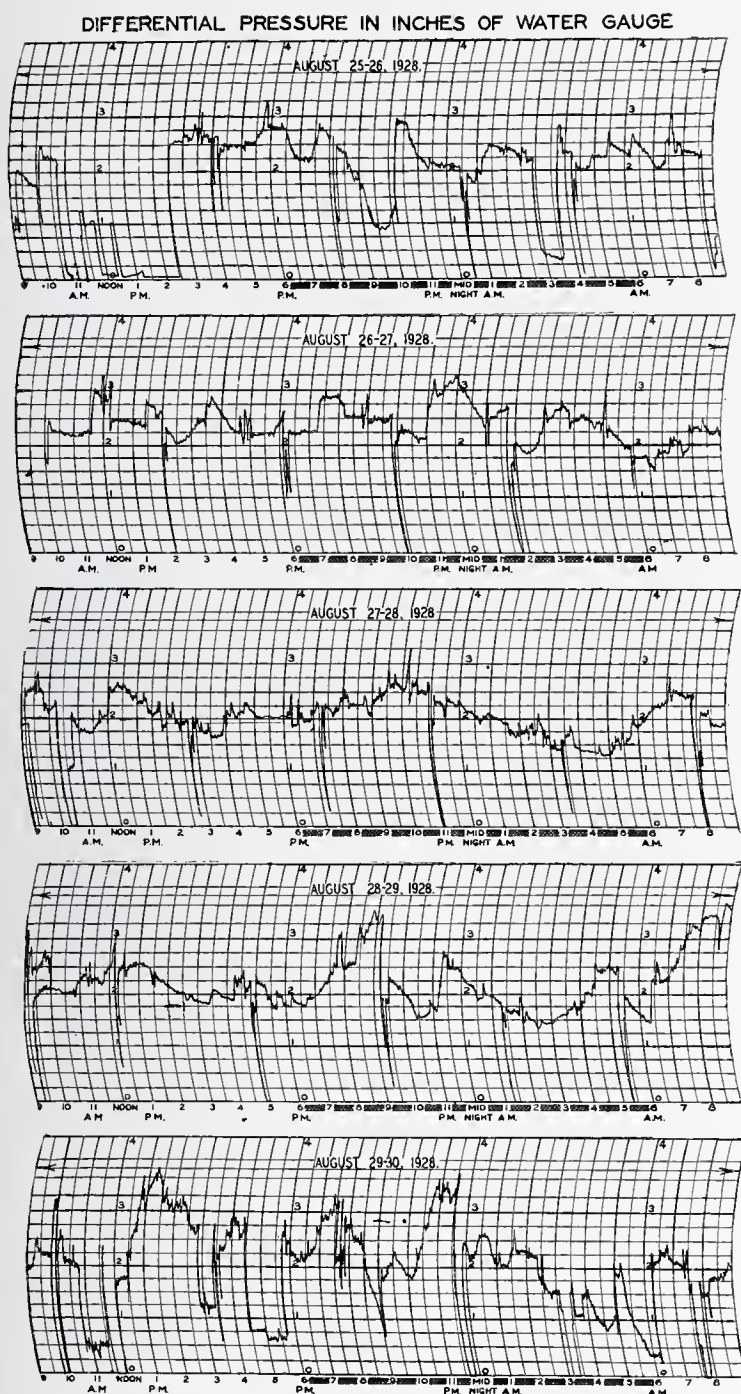


FIG. 7A. CHART OF DIFFERENTIAL PRESSURE READINGS  
Balanced manometer. Location—No. 3 Blast Furnace

- (4) Moisture in blast.
- (5) Shatter test of coke.

Figure 7 gives the chart of differential pressure readings indicative

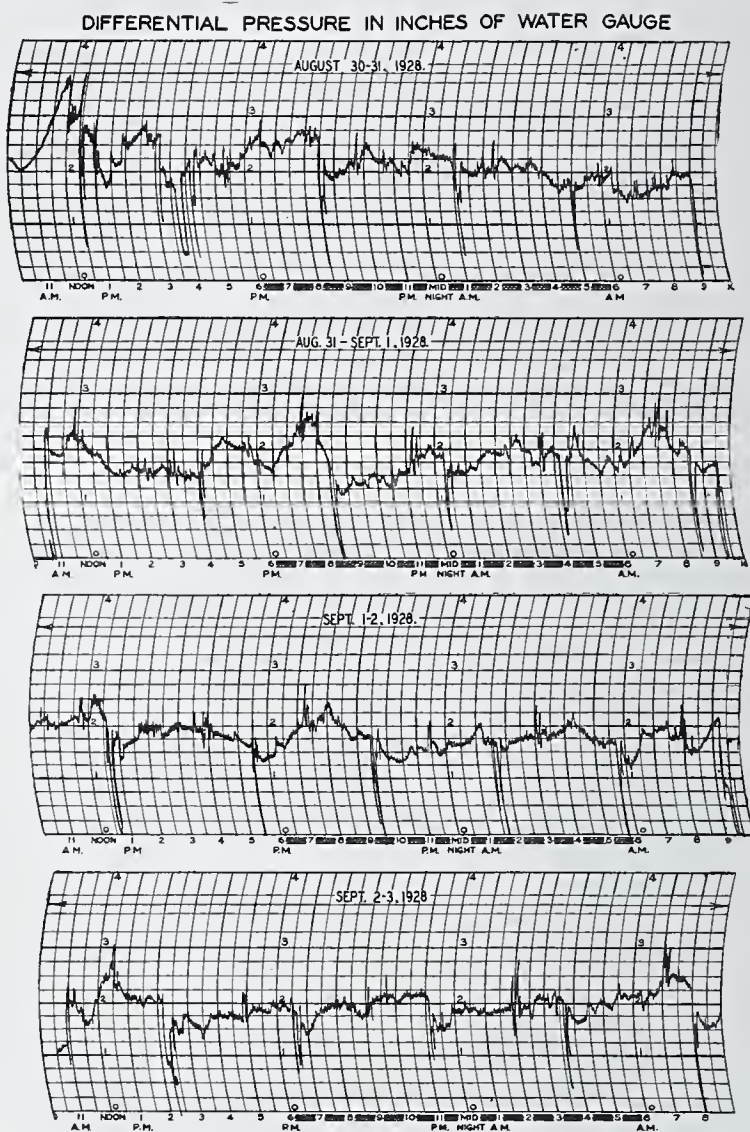


FIG. 7B. CHART OF DIFFERENTIAL PRESSURE READINGS  
Balanced manometer. Location—No. 3 Blast Furnace

of the weight of carbon burnt at the tuyeres during a period of operating difficulties. Apparently when the furnace is working normally, there is a small regular fluctuation in the volume of air

passing through the tuyeres per minute, suggesting that the material reaches the hearth by a series of small slips. If, however, any abnormality is introduced, the fluctuations become more violent, the slips become greater and unless the movement is checked the furnace is soon in difficulties as shown in the graph between the dates September 28 and September 30. If so, it would appear probable that any factor which would alter in any way the rhythmic operation of the furnace would tend to accentuate the slips, ultimately causing derangement of operation, reducing the efficiency of contact between gas and ore, increasing the fuel consumption and reducing the output.

These results were obtained at a well-managed furnace operating under constant pressure conditions and it would be of interest to know whether similar effects have been observed in furnaces operating under constant pressure blowing.

Uniformity of conditions of operation, is evidently of the greatest importance, but much further work is desirable before the many variables involved can be completely isolated one from the other and their effects on the furnace economy evaluated. Data for furnace operation under widely varying conditions obtained from studies of characteristic curves developed from volume measurements of this type would be of considerable assistance, particularly if they could be directly plotted against variables in normal operation. Some information has been obtained by statistical investigation of records available, and evidence is available of the effect of the following factors which directly effect the efficiency of contact between gas and ore.

- (1) Distribution of burden.
- (2) Method of charging.
- (3) Sizing of materials.
- (4) Furnace lines.
- (5) Coke quality.

Other factors which do not influence efficiency of contact but which also play a part are

- (6) Reducibility of ore—which affects the rate of reaction between ore and gas.
- (7) Moisture in blast, whose action appears to be two-fold, namely:
  - (a) Reduction of heat production per unit of carbon at the tuyeres due to endothermic reaction.



- (b) Its influence on the rate of reaction between ore and gas due to some unexplained effect of hydrogen and/or water vapor.

The effects of these factors have been studied in some cases by noting the alteration of furnace operation by introducing variables of a sufficiently large order to allow of quantitative measurement. In other cases, studies have been made of groups of furnaces having one factor in common, whose performance as a group differs widely from the mean, due probably to the influence of the common factor.

The following brief notes of some results available may serve to define more clearly the problems that have to be faced, and possibly in some cases to suggest a method of solution.

#### DISTRIBUTION OF BURDEN—METHOD OF CHARGING—SIZING

The practical results of distribution of materials in blast furnace practice are well known, but probably the most interesting recent work on the question deals with the effect of elimination of fines and the use of sinter. German furnaces using sinter have attained a production of 400 pounds of iron per square foot hearth area per hour as compared with average practice in the United States of 200 to 250 pounds. In cases where fuel economy has been aimed at, similar improvements have been effected. In certain cases quoted by H. J. Bush<sup>8</sup> a saving of 4 cwt. of coke per ton pig iron was effected by increasing the percentage of agglomerate fines in the burden from 13.4 to 28.4 per cent. Results of this character might be expected owing to the increased efficiency of contact between gas and ore with consequent increase in output or decrease in the X factor, but it is possible also that chemical phenomena connected with the carbon deposition reaction may have contributed to the results.

#### INFLUENCE OF COKE QUALITY

Similar results, but perhaps not so marked in character, have been obtained when coke fines are eliminated. Coke technology however, still offers a number of unsolved problems. One is the necessity for a standard test or series of tests for determining the physical value of a coke for blast furnace purposes. The shatter test is useful when wide divergencies exist. For example, the values obtained by R. A. Mott on cokes from different districts in Great Britain (Table

<sup>8</sup> *Jour. Iron and Steel Inst.*, Vol. I, 1928, p. 134.

II), probably represent blast furnace values of the coke used, other factors being equal.

In cases however, where shatter indices approach one another more closely and the cokes are made from coals of the same district, results are not so reliable. It has been stated for example, that some Durham cokes with a shatter index of the order of 75, give better results in blast furnace practice than others of somewhat similar composition but with a shatter index between 80 and 85. Useful therefore, as the shatter test is, there seems to be room for a method which would differentiate more closely between cokes of somewhat similar character. In this connection, the method of determining coke reactivity to carbon dioxide, devised by workers of the Fuel Research Board,<sup>9</sup> may be useful. From the results obtained by this organization, there appears to be generally, a

TABLE II

DISTRICT	SHATTER INDEX, 2-INCH SCREEN
South Wales .....	91
Durham .....	72.6
Yorkshire .....	64.4
Derbyshire .....	45.1
Shatter index of Westphalian coke as a basis of comparison ....	88.4

correlation between reactivity of coke to carbon dioxide and the shatter index, a high reactivity being associated with low shatter index and if reactivity values of British cokes are plotted against shatter indices, there appears to be a general grouping of the coke into specific districts.

As the reactivity test is more delicate than the shatter test, it may be of value when results can be correlated with those of blast furnace operation, but sufficient evidence is not yet available to allow of its being generally adopted as a measure of coke quality. The test however, is of theoretical importance as it throws a light on the structure of coke, particularly in relation to the character of the coal from which it is produced, and fundamental work on this aspect of the question is now proceeding. The fundamentals involved are of importance in relation to the possibility of improving

<sup>9</sup> *Jour. Iron and Steel Inst.*, 1927, Vol. I.

coke quality. In this connection, carbonizing temperature, length of coking time, oven width, coal size and other conditions of carbonizing play an important part, whose influence must be investigated for each specific case.

Blending frequently offers attractive possibilities. For example, in the Saare, blending of coking coal with low temperature coke has effected a marked improvement in coke quality. The raw coal has the following ultimate analysis:

	<i>per cent</i>
Total carbon.....	86.6
H.....	5.28
S.....	0.51
O·N.....	7.35
Volatile matter.....	33.15

TABLE III

	ON 4 INCH	ON 3 INCH	ON 2 INCH	ON 1½ INCH	ON 1 INCH	ON ¾ INCH	ON ½ INCH	THROUGH ¼ INCH
Size analysis on receipt:								
Straight coke.....	24.4	42.6	61.8	72.9	86.8	97.1		
Blend coke.....	22.3	52.0	84.9	93.8	96.8	98.8		
Shatter tests:								
Straight coke.....			64.5	75.0	86.0	97.2		
Blend coke.....			80.0	92.7	97.3	98.7		
Abrasion tests:								
Straight coke.....			81.4	91.9	93.9	97.2	98.2	1.8
Blend coke.....			89.0	96.3	96.8	97.0	97.3	2.7

This in practice is blended with about 17 per cent of low temperature coke containing about 11.9 per cent of volatile matter.

The results of tests made by R. A. Mott on cokes from the raw and blended coal, carbonized in the same battery of coke ovens (Table III), indicates the improvement effected, while considerable economies have also been effected in blast furnace operation.

#### REDUCIBILITY OF ORE

The effect of ore quality is indicated in Figure 8 where results obtained from a group of furnaces using a similar ore are compared with averages from other districts. Similar conditions have been

noted in other producing centers. Apparently some ores require a minimum time of contact in the furnace to secure efficient reduction. If attempts are made to drive the furnace too rapidly, a rapid increase in the X factor results with a high fuel consumption. It is not

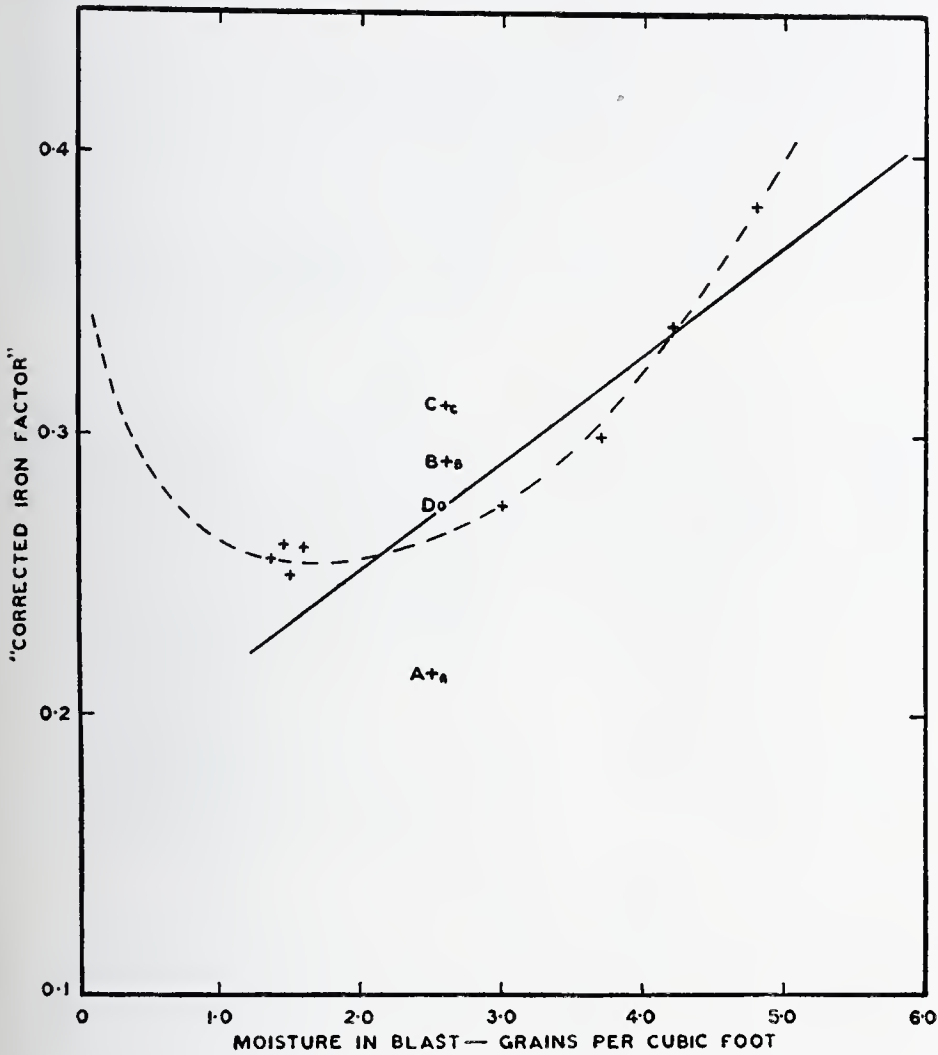


FIG. 8. SHOWING EFFECT OF ORE QUALITY

yet known whether this is due to the physical condition of the ore or to its chemical characteristics, and there is need for a method of evaluating ores for blast furnace use, which would take into consideration the time factor for efficient reduction.

The term "reducibility" is being used for the time being in this

connection but it is not yet certain that the phenomena observed are due to a low degree of reducibility or otherwise, as some of the ores giving anomalous results of the type reported are easily reducible and in some cases improvement has been effected by admixture of a proportion of "hard" ore, so that some quality other than reducibility may be playing a part.

The matter is at present being investigated on behalf of the National Federation of Iron and Steel Manufacturers of Great

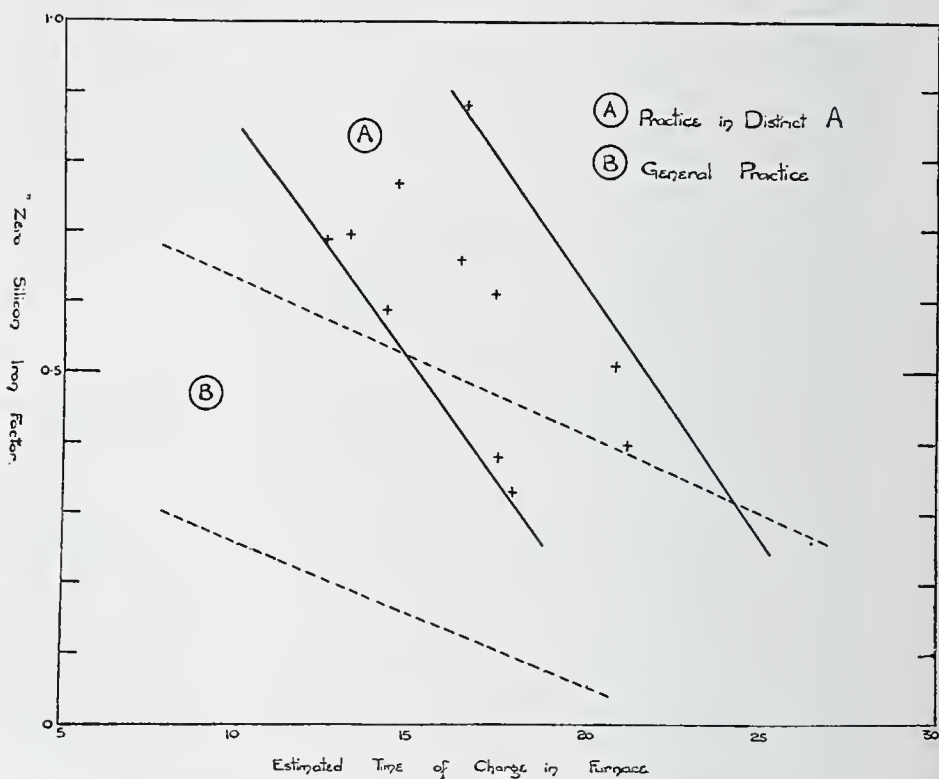


FIG. 9. GRAPH OF OPERATING RESULTS, WITH AND WITHOUT DRY BLAST

Britain by Prof. W. A. Bone and his collaborators and there is hope that the investigations in progress will throw a light on the subject. Phenomena connected with carbon deposition are apparently playing an important part, but the results available are as yet insufficient to allow of direct and specific application to blast furnace practice.

#### MOISTURE IN BLAST

A blast furnace has been in operation at Wishaw Iron and Steel Works for some time in which the blast is dehydrated with silica

gel. A study of the results obtained by Mr. E. H. Lewis with this plant, opens up some interesting speculations. Figure 9 gives a graph of operating results with and without dry blast, and this seems to indicate that there is an optimum degree of dryness of the order of 1.5 grams moisture per cubic foot of air to secure optimum efficiency. It would be anticipated from a knowledge of the extreme slowness at which chemical reactions proceed in absolute dryness, that there should be some minimum moisture content in the reacting gases, and this appears to be confirmed by recent experimental work by Professor Bone and his collaborators. A study of the results also shows that the practical effects on the fuel consumption are much greater than can be calculated simply from the thermal requirements for the equation



and apparently the presence of hydrogen and moisture in blast furnace gas has a marked retarding influence on the rate of the reactions involved. In this connection, the published work of W. A. Bone, L. Reeve and H. L. Saunders has shown that the addition of 2 per cent of hydrogen profoundly influenced the phenomena of reduction of ores examined at temperatures up to 550° and if this applies also to conditions at higher temperatures, the Wishaw results could be explained.

Investigations at temperatures above 600 are now in progress and it is hoped that results will throw a light not only on the phenomena observed in connection with dry blast, but also on other aspects of blast furnace technology.

### CONCLUSION

Generally, the subject is one which bristles with complexities and rapid though progress has been during the past few years, the field of investigation is widening rather than narrowing. The work of individual investigators in the United States and other countries, and by such organizations as the United States Bureau of Mines, the Fuel Research Board in Great Britain, the Wärmestelle, Dusseldorf, in Germany, and similar organizations in other countries, is particularly helpful, not only in the light that their researches throw on the fundamental problems involved, but also in the authentic data of operation which they are, in virtue of their centralized position able to collate and co-ordinate.

An examination of such data frequently allows as results accumulate, of statistical surveys being made, which are helpful in correlating results of fundamental research with those of practical operation.

Similar methods of analysis could be applied to other aspects of iron and steel practice, provided the data were available. Investigation, for example, of the fundamentals of open hearth practice by thermal analysis, would be particularly helpful, as the biggest factor involved is the fuel consumption to meet radiation and other external cooling losses, but while information regarding operating practice is growing, it is as yet still insufficient to allow of detailed analysis.

The deductions submitted in these notes cannot be regarded as final. Based as they are on a limited number of operating results, they can only be considered as an actuarial average of results examined, which, as data accumulates is open to modification. Still, it is hoped that sufficient evidence has been given of the value of publication of international data regarding iron and steel practice, with a view to its ultimate analysis. Studies of practice, widely divergent in character and covering extreme ranges, are particularly helpful in that they may allow of the isolation of factors which may predominate under extreme and special conditions, and thus indicate possibilities of improvement in practice which would be international in their ultimate effects on the efficiency of the industry.

## THE HEAT EXPENDITURE IN THE COKING PROCESS

By ERNEST TERRES, DR. ING.

*Professor in the Technische Hochschule, Braunschweig*

Fuel economy is one of the important demands in all countries. Most industries especially in Germany have introduced in the last decade heat research laboratories for determining the efficiency of the most varied types of furnaces from the calorific point of view, and for undertaking measurements and suggesting improvements in the economical use of heat.

Our particular industry, the production of coke and gas in coke plants and gas works, belongs to the industries that consume the most fuel. In consequence, the necessary expenditure of heat for the transformation of coal into coke forms at present the center of the discussion.

The determination of this expenditure of heat has limited itself until now to the measurement of the actual fuel consumption of the existing ovens. We limited ourselves to the determination of the overall efficiency of the ovens. Oven design is still based on empiricism. Until now a knowledge of the underlying scientific facts needed to determine the theoretically required heat expenditure and also the net efficiency of the coke and gas plants ovens has been lacking.

During the last few years with several collaborators I have devoted myself particularly to these questions and we have advanced quite a bit in the theoretical knowledge of them. I should like to inform you concerning the principal results of our studies.

Modern oven construction in the gas and coke industry has always considered one of its chief aims to be to reduce as much as possible the expenditure of heat necessary for coking. In this the determination of the fuel consumption was based exclusively on experiences in operation. I should like to report first of all on the actual heat consumption prevalent in large plants, before I come to my real subject. In doing this, it is advisable to make a distinction between gas plant ovens and coking ovens. Let us begin with the former.

The fuel consumption is very different for different types of ovens. In the case of intermittently operated ovens with integral gas producers and air preheating in recuperators, we assume an average

heat expenditure of 12 kgm. of coke free of moisture and ash per 100 kgm. of air-dried coal. This allows for the efficiency of the producers and corresponds to a total expenditure in calories of 955 kcal. per kilogram of coal. The lowest expenditure of heat up to date amounts to 11.5 kgm. of coke free of moisture and ash per 100 kgm. of air-dried coal or 935 kcal. per kilogram of coal. If one admits a producer efficiency of 75 per cent the heat requirement amounts to 715 to 685 kcal. per kilogram of coal calculated in calories in the form of heating gas at the oven.

Ovens heated by gas coming from outside sources, especially by producer gas, and having recuperative gas and air preheating, require 650 kcal. per kilogram of air-dried coal figured in heat units in the form of fuel gas at the oven. In this, fuel gas with a higher heat value shows itself somewhat more efficient than the usual lean gas from producers.

In the case of continuously operated ovens with recuperative air and gas preheating, the fuel consumption is somewhat less; it fluctuates between 580 to 560 kcal. per kilogram of coal.

For gasification by steam standards have been fixed in Germany for the permissible fuel consumption including the efficiency of the producer, and the permissible heat requirement has been graded according to the number of cubic meters of produced water gas. We have accepted as permissible maximum limits:

	<i>kgm. pure coke</i>
For dry distillation per 100 kgm. of coal.....	12.0
For each of the first 5 cbm. water gas 0.1 kgm. pure coke.....	0.5
For each of the second 5 cbm, water gas 0.15 kgm.....	0.75
For each of the third 5 cbm. water gas 0.2 kgm. pure coke.....	1.0
	<u>14.25</u>

That is, for a gas yield of 48 to 50 cbm. per 100 kgm. of coal, a fuel consumption of 14.25 kgm. of pure coke is permissible: or expressed in heat units per kilogram of coal  $\frac{14.25 \times 7950}{100} = 1133$  kcal., and in case of 75 per cent producer efficiency, in round numbers 850 kcal. per kilogram of coal.

These numbers hold for the ovens of gas works.

The coking industry has always calculated with a lower expenditure of fuel and has really attained it. This lower consumption is caused partly by lower heat losses from conduction and radiation with horizontal ovens, partly by the use of fuel gas of a greater calorific

value (coal gas), and partly by a better efficiency of the heat salvage equipment. As a rule all coke ovens have regenerative air preheating, and by heating with lean gas a regenerative gas and air preheating. The fuel consumption of coke ovens fluctuates as a rule between 540 to 580 kcal. per kilogram of air-dried coal expressed as heat units in the form of fuel gas at the ovens; however we succeeded in the most modern plants with narrower and higher chambers respectively, and with gradual heating in large plants, in reducing the heat consumption to 420 to 480 kcal. per kilogram of air-dried coal.

These last figures were first considered impossible and attributed to errors in testing, since the theoretical heat requirement for the coking process, that is the coking heat, was considered to be higher.

We understand by coking heat that amount of heat in kcal. which must be used in order to transform 1 kgm. of air-dried coal at 20°C. into coke at any definite temperature, including the energy in kcal. which corresponds to the external work performance of the gaseous products of distillation.

This coking heat should not be confused with the heat of decomposition of coal in the coking process. We understand by heat of decomposition the heat phenomena occurring in the coal upon being transformed into coke, which may consume as well as develop heat. The latter has to do with the coking heat only in so far as they increase or diminish its magnitude in the range of temperature in question. We shall illustrate that later with curves.

While the heat of decomposition has more theoretical importance, the coking heat is of practical value. The fuel consumption actually required in an oven for the transformation of the coal into coke is composed of the coking heat of the coal, the losses of heat by radiation and conduction of the oven and the sensible heat losses in the flue gas. The knowledge of the coking heat makes possible the calculation of the net efficiency of the coke oven, as well as of its losses by radiation and conduction.

In the last three years we have studied these questions thoroughly and we have developed a method of determining the coking heat of any coal which is accurate to plus or minus 1 per cent. At the same time the measurements may be so arranged that the heats of decomposition for any temperatures can also be obtained from them.<sup>1</sup>

<sup>1</sup> E. Terres u. H. Wolter, *Gas- und Wasserfach*, 1927.

E. Terres u. M. Meier, loc. cit., 1928.

E. Terres u. K. Voituret, loc. cit., 1928.

By the normal coking heat and the normal decomposition heat we understand the amounts of heat corresponding to the coking at 1000°C. The coking heats at temperatures up to 600°C. should be called charring heat (in German—Schwelwärme). They are of importance for the low temperature coking of coal as well as the distillation of lignite. I shall not discuss lignites at all in this paper.

The heat of coking of coal was measured about fifteen years ago by C. Otto. He carried out the coking in an electrical tube oven of special construction, which was surrounded on the outside by a cooling waterjacket, so that it had at a constant inner temperature a constant flow of heat outwards and therefore in a unit of time also equal heat losses by conduction and radiation. His method consisted in determining these heat losses for constant inner temperatures and calculating the heat of coking from these heat losses by measuring the electrical energy that was necessary to compensate for the drop in the temperature caused by a definite amount of coal in the same electrical oven, which had previously been brought to a definite temperature. The differences between the heat needed for this compensation in the form of electrical energy and the previously determined losses of heat by conduction and radiation, he considered as coking heat. Considering the smallness of the coking heat to be measured, his method is too involved and inaccurate: the values established by Otto are according to our present experiences too high by 70 to 100 per cent. With an increasing coking temperature he finds a regular increase of the coking heat and it is surprising that all kinds of coal, investigated by him exhibit also negative decomposition heats of great magnitude. In order to give you an idea of the size of the numbers found by him, it is sufficient to say that in all his experiments the coking heat was found to be at about 730°C. on the average of 600 kcal. and at about 1000°C. on the average of 750 kcal. per kilogram of air-dried coal.

Our method of measuring the coking heat of coals is the following: a receptacle of quartz is set in a calorimetric bomb and heated up to temperatures of 1100°C. by electric energy. Through ingeniously attached insulation cylinders we succeed in using the greatest part of the electric energy to heat the system and to execute the coking process, so that only the smaller part of it flows into the calorimeter during the heating. I cannot explain here the details of the method of working, and it will be sufficient to know that the coking heat is found as the difference between the total heat sent into the system

in the form of electric energy and the quantity of heat that goes into the calorimeter during the heating up to the maximum of the temperature in the coking receptacle plus the heat content of the empty

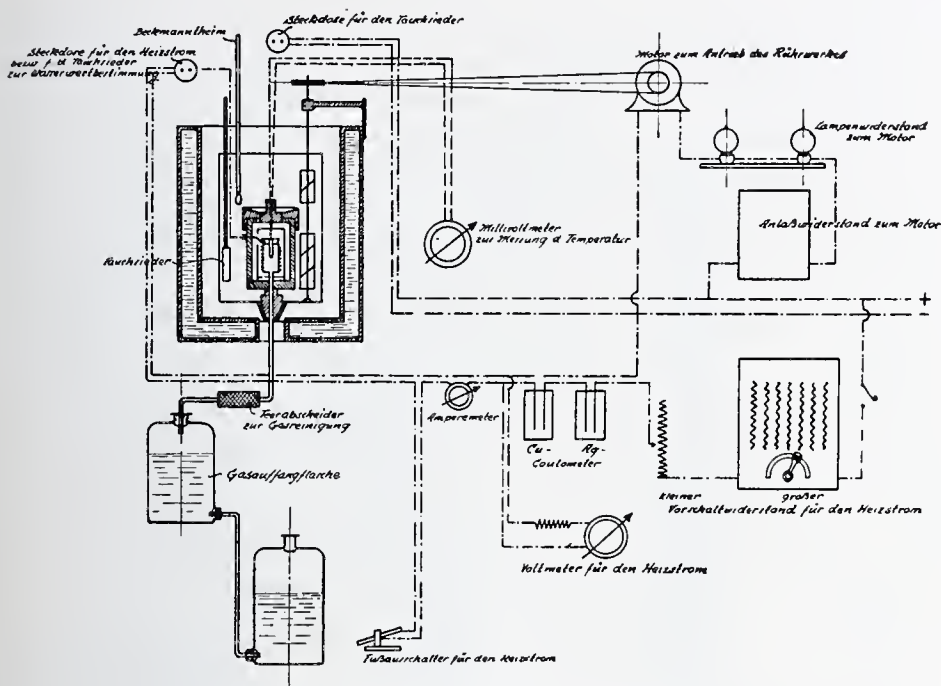


FIG. 1. GENERAL DIAGRAM OF CALORIMETRIC APPARATUS

*Beckmanntherm* = Beckmann thermometer.

*Steckdose für den Heizstrom bzw. f.d. Tauchsieder zur Wasserwertbestimmung* = wall plug for the heating current or for the immersion heater used for the determination of the water equivalent.

*Steckdose für den Tauchsieder* = wall plug for the immersion heater.

*Tauchsieder* = immersion heater.

*Millivoltmeter zur Messung d. Temperatur* = millivoltmeter to measure the temperature.

*Motor zum Antrieb des Rührwerkes* = motor for driving the stirring apparatus.

*Lampenwiderstand zum Motor* = lamp resistance for the motor.

*Anlasswiderstand zum Motor* = starting resistance for the motor.

*Teerabscheider zur Gasreinigung* = tar eliminator for gas purification.

*Gasauffangflasche* = gas receiving flask.

*Amperemeter* = ammeter.

*Cu-Ag-Coulometer* = Cu.-Ag. coulomb meter (voltameter).

*Verschaltwiderstand für den Heizstrom* = rheostat for the heating current.

*Voltmeter für den Heizstrom* = voltmeter for the heating current.

*Fussausschalter für den Heizstrom* = foot switch for the heating current.

system at the coking temperature in question. But the supposition for an unequivocal calibration of the system is dependent on the condition that the system will be saturated with heat at every coking

temperature in question. The calibration of the apparatus is difficult to effect, but the measurements are today not essentially more complicated than a simple determination of the combustion heat of fuels.

I show you in Figure 1 the schematic drawing of the measuring apparatus. The bomb in which is built the coking receptacle with a heating equipment is placed in a large calorimeter. The coking receptacle, Figure 2, is of quartz and has in its bottom a delivery tube for the gaseous products of distillation, which are collected after being

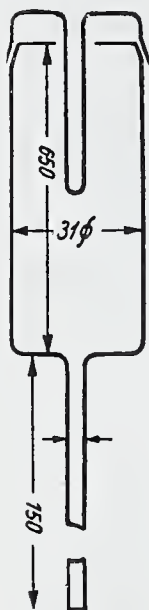


FIG. 2. THE  
COKING  
RECEPTACLE

freed from the vapors of tar and water by cooling. The volume of the gaseous products of distillation will be determined, as well as the composition of the gas, the heat value of it and the calorific value. The coking vessel is closed by a quartz cover ground on, which has a tube closed on one side that permits insertion of the thermo-element for measuring the temperature in the center of the coke. The tests are effected with 12 to 15 grs. of coal.

In this way we find the coking heat of a coal for any coking temperature up to about 1100°C.

A simple variation of the apparatus enables one to secure all numerical data for the simultaneous determination of the decomposition heat of any coal at any distillation temperature. For this it is sufficient to know only the heat content of the gaseous products of distillation including the condensing heat of the tar and water vapor, which is measured separately in a second calorimeter. The heat of decomposition results thereby as the difference between the coking heat at the temperature in question, and the sum of the real heat content of the coke (calculated from the coke yield, the coking temperature and the mean specific heat values) the real heat content of the gaseous products, the heats of condensation of tar and water vapor included (determined by experiment) and the performance of work of the gaseous products against the external atmosphere, expressed in thermal units. The latter value amounts according to the quantity of gaseous products to 4 to 11 kcal. per kilogram of air-dried coal and this number must not be neglected.

You see in Figure 3 a schematic sketch of the measuring apparatus, as it is used for the simultaneous determination of the heat of coking

and of decomposition of coal. In reality the apparatus is the same as the first photograph represented it, only a second calorimeter has been added for the measuring of the heat content of the gaseous

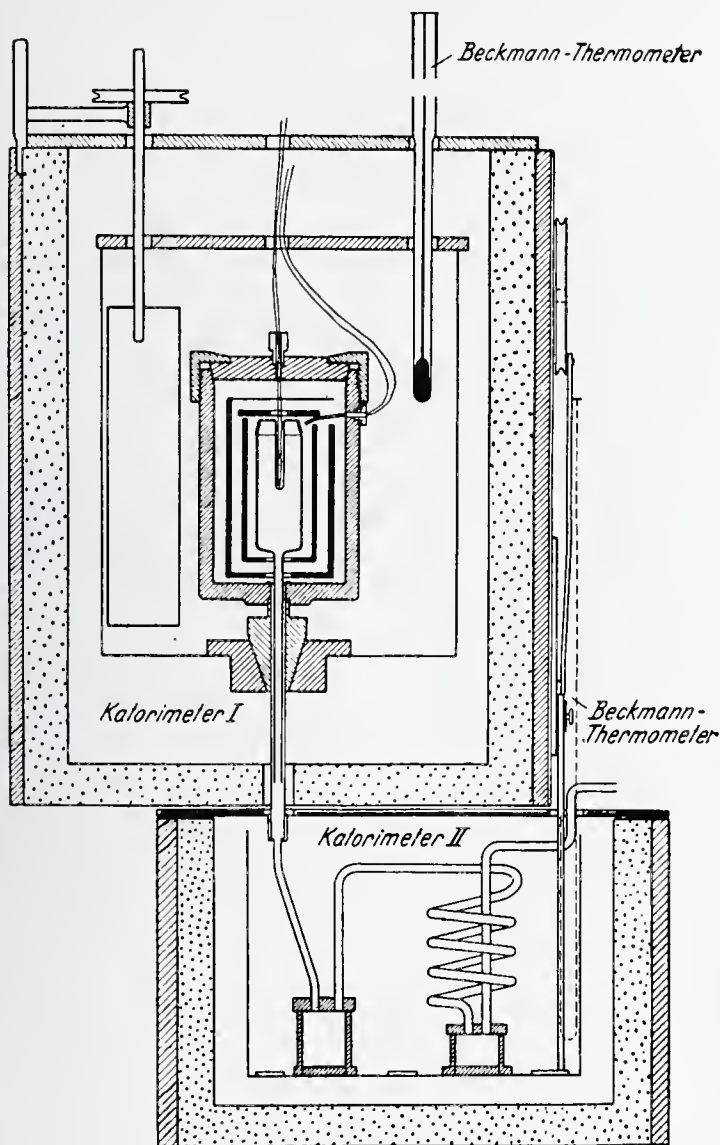


FIG. 3. SCHEMATIC SKETCH OF CALORIMETER

products of distillation including the condensation heat of tar and water vapor. The time is too short to show you more details; it will be sufficient to say that this method is now developed to such

an extent that the inaccuracy of the results does not exceed plus or minus one per cent.

Before us, other ways have been attempted to determine the decomposition heat of coals by experiment. Mahler was the first to try 35 years ago to find out by experiment if the coking process at about 1000°C. is accompanied by heat phenomena. Mahler based the determination of this decomposition heat upon the thought that in the case of any sort of heat phenomena the total heat of combustion of a coal is distributed quantitatively among the different products of distillation, as coke, tar and gas, and it must be equal to the sum of these different heats of combustion; in the case of an evolution of heat during the coking process the sum of the different heats of combustion would have to be smaller by this same amount of heat and in the case of a heat absorption during the coking process the sum ought to be larger by this same amount of heat than the heat of combustion of the coal. The heat of decomposition of a coal is found consequently by the determination of the different heat values of the coal, the coke, the tar and the gas. The difficulties of this measuring method are caused by the impossibility of measuring correctly the quantity of the products of distillation. He determined in this way from carefully conducted investigations with coal of Commentry a rather large evolution of heat during the coking process amounting to 254 kcal. per kilogram of air-dried coal, a value which is too high by about 400 per cent as we know at present.<sup>2</sup>

By the same method measurements have been made by Poole<sup>3</sup> and later by E. J. Constam and P. Schlaepfer<sup>4</sup> and by myself;<sup>5</sup> all these measurements showed large fluctuations and the values found were about of the same order of magnitude as the result of Mahler.

In another way, but not less hard and complicated, Euchène<sup>6</sup> of the Compagnie Parisienne d'éclairage et de chauffage par le gaz has determined the decomposition heat of coals by careful researches which were conducted on a large scale. His method was based upon the idea that the total heat of the fuel consumption distributes itself among:

1. The sensible heat of the gaseous products of distillation,

<sup>2</sup> *Bulletin de la Societe d'encouragement pour l'industrie nationale*, 1893.

<sup>3</sup> *The American Gaslight Journal*, 1898, Heft 4.

<sup>4</sup> *Journal f. Gasbeleuchtung u. Wasserversorgung*, 1906, 741 u. ff.

<sup>5</sup> *Ruhrkohle und Technik*, 1928, S. 133.

<sup>6</sup> *Compagnie Parisienne d'éclairage et de chauffage par le gaz*.

2. The sensible heat of the flue gases,
3. The sensible heat of the incandescent coke,
4. The loss of heat by conduction and radiation of the oven,
5. The heat loss in the clinkers of the gas producer, and
6. The negative reaction heat during the coking process.

The positive or negative heat of decomposition of the coal in question is found as the difference of the sum of these heat quantities and of the heat in the fuel needed for heating the oven.

The exact execution of the method of Euchène is still more difficult than Mahler's method. Nevertheless the results of the tests with three different French coals lie absolutely in the order of magnitude of the values determined at present by more accurate methods. Euchène found with a coal, number one, a heat of decomposition of about plus 12.39; for a coal, number two, plus 35.98; and for a coal, number three, plus 63.51 kcal. per kilogram of air-dried coal.

The direct determination of the heat of decomposition of coals by experiment has been effected by F. D. Davis<sup>7</sup> and F. F. Byrne and by H. Strache and H. Grau,<sup>8</sup> each by a different method.

Davis and Byrne used a double calorimeter, each of which contained exactly the same calorimetric bomb with exactly the same interior equipment. In one of these bombs 1 gram of coal is transformed into coke, whereby each calorimeter is heated up with exactly the same quantity of heat, in such a way, that the inner temperature reaches about 500°C. From the different behavior of both calorimeters the heat of decomposition of the coal in question is calculated. Ten kinds of American coal have given the result that the heat of decomposition is positive, that is, there is an evolution of heat, which corresponds on the average to an amount of plus 30 kcal. with an inaccuracy of plus or minus 1 kcal. per kilogram of air-dried coal. Notable is their observation that coal shows reactions with evolution of heat only in the range of temperature up to about 650°C. and that the evolution of heat is the largest at about 500°C. while above this range the heat of decomposition becomes more and more negative. These observations do not prove true for the approximately four dozen German and English coals investigated by us up to now, as I shall show you later by curves. After all, Davis and Byrne may have been the first to have determined with sufficient accuracy the decomposition heats of coal according to magnitude, but the number

<sup>7</sup> Bureau of Mines, Pittsburgh.

<sup>8</sup> Brennstoffchemie, 1921.

of kinds of coal chosen by them is not sufficient in order to derive a rule or, as the case may be, to generalize upon the results.

The method of H. Strache and H. Grau is not as accurate as the one just described. They experimented likewise with a calorimetric bomb, in which was built an electric oven in the interior copper receptacle of which the coking was carried out with 1 gram of coal. The determination was effected in such a manner that the total amount of heat was determined which had gone into the calorimeter during the heating up to the coking temperature and after shutting off the electrical current and during the recooling to the calorimeter temperature. The difference of this amount of heat compared with the total heat sent in in the form of electrical energy represents the positive or negative decomposition heat of the fuel in question. The measurements show considerable fluctuations but the average values lie in acceptable orders of magnitude. They found for two kinds of coal the decomposition heat of minus 8 kcal.; for two lignites plus 49 and plus 51 kcal. respectively; for cellulose plus 230 kcal.; and for wood plus 231 kcal. per kilogram of material.

All these measurements show that the coking process is accompanied by positive or negative heat phenomena and that the heats of decomposition of coal do not reach nearly such considerable amounts as have been accepted until now.

In reality, however, conditions are still more complicated, in that the heat phenomena of the reactions of the coking process change with the coking temperature; that reactions with positive and negative heat phenomena alternate in the ranges of temperature up to 1000°C., and that with high temperature positive decomposition heats may still occur. Accordingly the measured heats of decomposition at the various coking temperatures are the differences between the reaction heats of the exothermic and endothermic reactions occurring simultaneously or successively. Our method in contrast to the former gives the decomposition heat curve for the total temperature range up to about 1100°C.

I want to show you now with the aid of several curves the variation of the coking heats and decomposition heats of several kinds of coal as a function of temperature and I want to discuss the importance of these values for the evolution of coals, as well as for the determination of the fuel consumption and for the calculation of the coking time of different coals in chambers of different widths. The curves of five different coals will suffice. These are a gas coal from each, the

Saar and Ruhr districts, two coking coals from the Ruhr district and an English gas coal of the Boldon district.

As a specimen of Saar coal I have chosen the Heinitz-Dechen coal which is the testing coal par excellence for determining the efficiency of ovens.

Figure 4 shows the coking heat curve for the temperature range from about  $600^{\circ}$  to  $1070^{\circ}\text{C}$ . At first glance the form of the curve is surprising since with increasing coking temperature also a constant increase of the heat consumption is to be expected. That is not the case here; the form of the curve is caused by the decomposition reactions occurring at the time of coking with partly positive and partly negative reaction heats. Between  $600^{\circ}$  and about  $750^{\circ}\text{C}$ . the

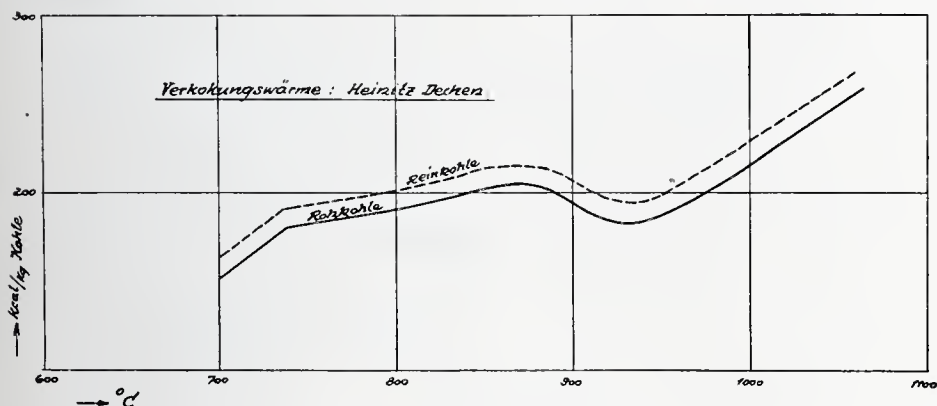


FIG. 4. COKING HEAT CURVE. TEMPERATURE RANGE ABOUT  $600^{\circ}$  TO  $1070^{\circ}\text{C}$ .

*Verkokungswärme* = coking heat.

*Reinkohle* = pure coal.

*Rohkohle* = crude coal.

coking heat is almost constant with about 175 kcal. per kilogram of air-dried coal; then with increasing temperature to about  $870^{\circ}\text{C}$ . the coking heat rises to about 206 kcal., and at  $930^{\circ}\text{C}$ . it passes through a minimum with 184 kcal. and from there on it rises in a straight line with increasing temperature. The normal coking heat at  $1000^{\circ}\text{C}$ . amounts to 217 kcal. per kilogram of air-dried coal. I should like to remark here that Saar coals are among the coals that require the least amount of heat for coking, but that on the other hand, as I shall show later, on account of the swollen and porous coke, the thermal conductivity is smaller and consequently the difference in coking time is not so great in comparison with other coals having a higher coking heat as would be expected from the low expenditure of heat for coking.

The curve, Figure 5, shows the decomposition heat curve of the same coal. You will see that the coking process in the whole range of temperature is accompanied by reactions of positive reaction heat.

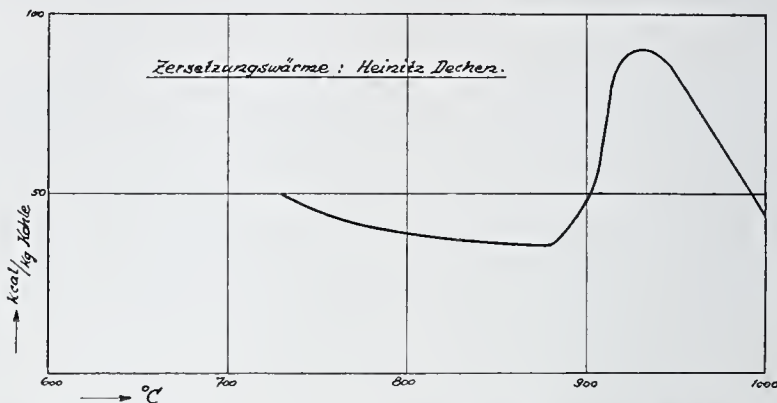


FIG. 5. DECOMPOSITION HEAT CURVE FOR HEINITZ-DECHEN COAL  
Zersetzungswärme = heat of decomposition

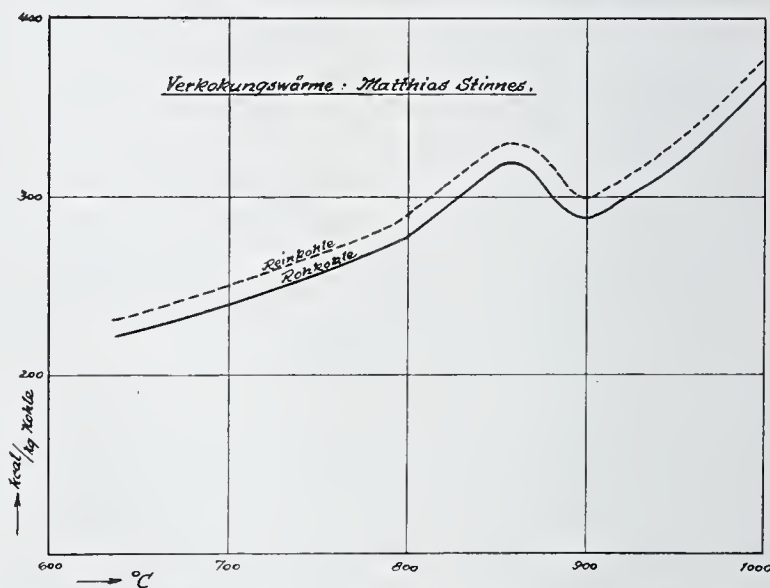


FIG. 6. COKING HEAT CURVE FOR MATHIAS STINNESS COAL  
Verkokungswärme = coking heat.  
Reinkohle = pure coal.  
Rohkohle = crude coal.

The heat of decomposition decreases between 730° and 880°C. from plus 50 to plus 34 kcal. per kilogram of coal and then at 930° with plus 91 kcal. reaches a maximum whereupon a quick decrease follows

again to zero kcal. at about  $1060^{\circ}\text{C}$ . At  $1000^{\circ}\text{C}$ . the decomposition heat is positive with plus 50 kcal. per kilogram of coal.

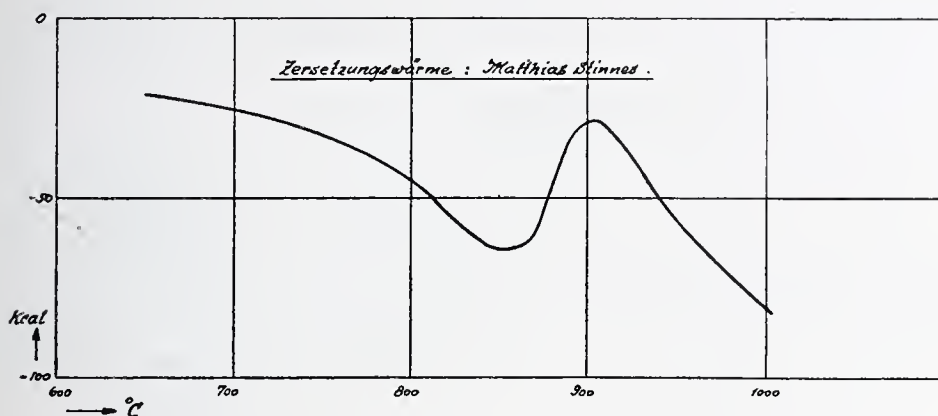


FIG. 7. DECOMPOSITION HEAT CURVE FOR MATHIAS STINNESS COAL  
Zersetzungswärme = heat of decomposition

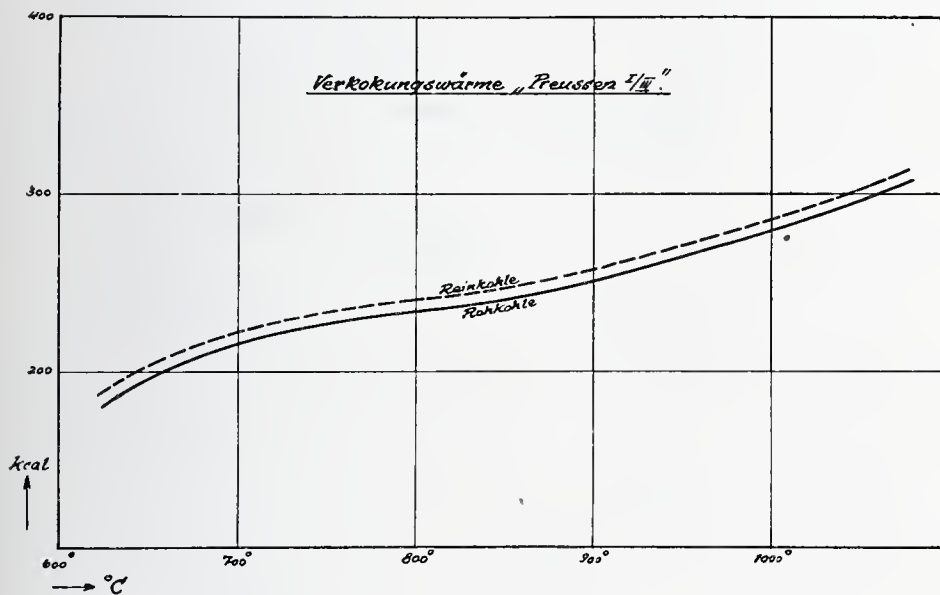


FIG. 8. COKING HEAT CURVE FOR PREUSSEN COAL

Verkokungswärme = coking heat.

Reinkohle = pure coal.

Rohkohle = crude coal.

Figure 6 shows the coking heats of the Ruhr gascoal called Mathias Stinnes coal. The coking heat lies considerably higher than the Saar coal in the whole range of temperature from  $600^{\circ}$  to  $1000^{\circ}\text{C}$ .;

it increases from about 240 kcal. at 700° to 370 kcal. at 1000°, with a minimum at 900° with 290 kcal.

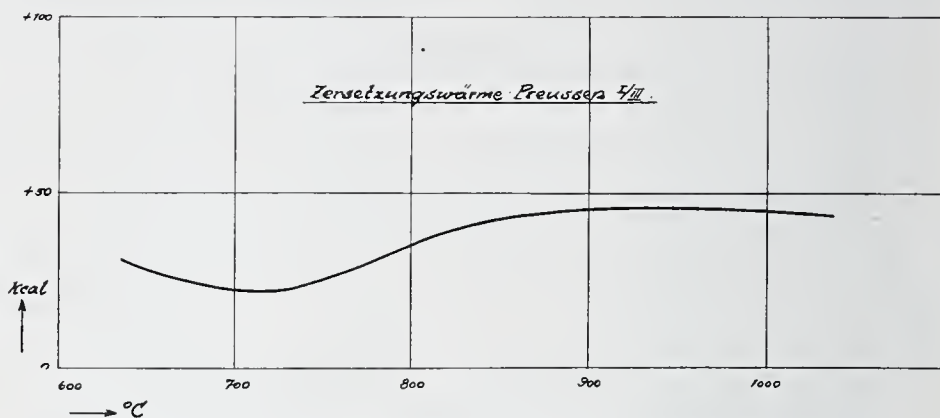


FIG. 9. DECOMPOSITION HEAT CURVE FOR PREUSSEN COAL  
Zersetzungswärme = heat of decomposition

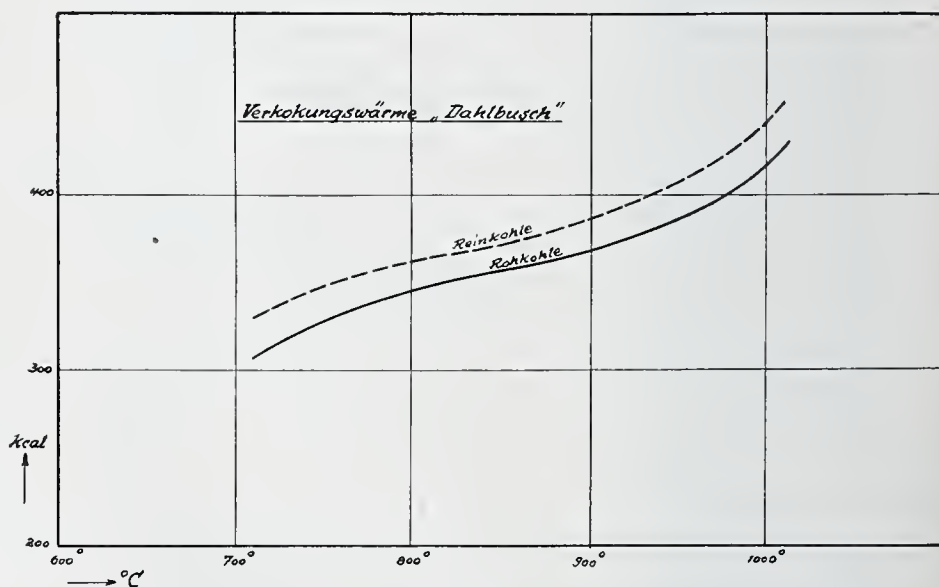


FIG. 10. COKING HEAT CURVE FOR DAHLBUSCH COAL  
Verkokungswärme = coking heat.  
Reinkohle = pure coal.  
Rohkohle = crude coal.

This coal however has the peculiarity that the decomposition heat in the whole range of temperature is negative. Apart from a maximum in the curve, Figure 7, of decomposition heat at 910°C. with

minus 36 kcal. the values drop from minus 26 kcal. at 860° and reach in round numbers minus 100 kcal. at 1000°C.

I should like to cite further the results of two coking coals. The coal of the mine Preussen shows with regard to the coking heats a sharply climbing, almost rectilinear curve, Figure 8, which begins at 620°C. with 180 kcal. and reaches at 1080°C. the value of 308 kcal. The coal has in the whole range of temperature a positive decomposition heat, Figure 9, increasing from plus 31 kcal. at 625° to plus 45 kcal. at 1000°C.

The Dahlbusch coke coal of the Ruhr district has the highest coking heats which we have found up to now, and it is known to be difficult to transform into coke in coke ovens. The curve, Figure 10,

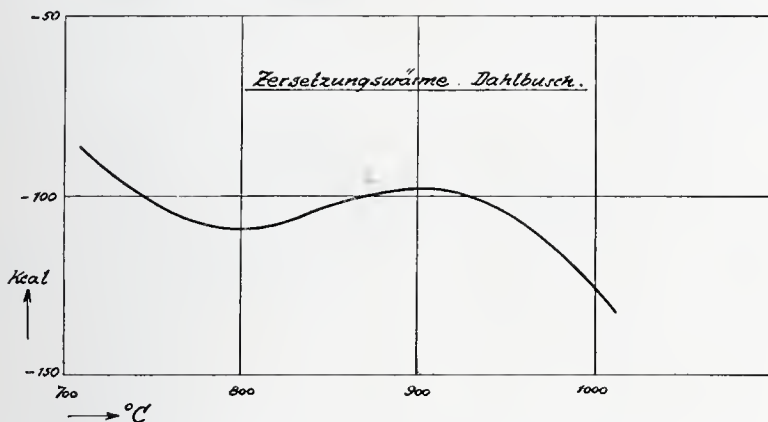


FIG. 11. DECOMPOSITION HEAT CURVE FOR DAHLBUSCH COAL  
Zersetzungswärme = heat of decomposition

ascends from 700° to 1000° from 310 kcal. to 420 kcal. per kilogram of air-dried coal.

In harmony with these results the decomposition heat in the whole range of temperature is considerably negative so that even at 700°C. it amounts to minus 95 kcal., Figure 11, and continues to diminish until it reaches approximately the value of minus 140 kcal. at 1000°.

In conclusion let us mention the results with the English coal Easington of the Bolden district which is also known in practice as being difficult to convert into coke and which requires a very long time for coking. In harmony with these experiences are the values of coking heat, Figure 12 which point to the peculiar qualities of this coal. Up to 930°C. the coking heat is remarkably low with a mean

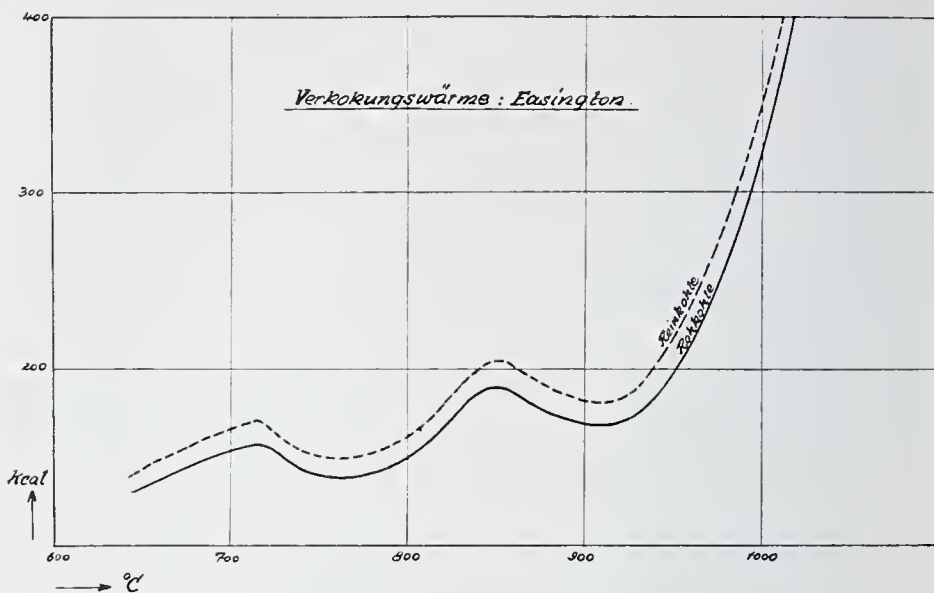


FIG. 12. COKING HEAT CURVE FOR EASINGTON COAL

*Verkokungswärme* = coking heat.

*Reinkohle* = pure coal.

*Rohkohle* = crude coal.

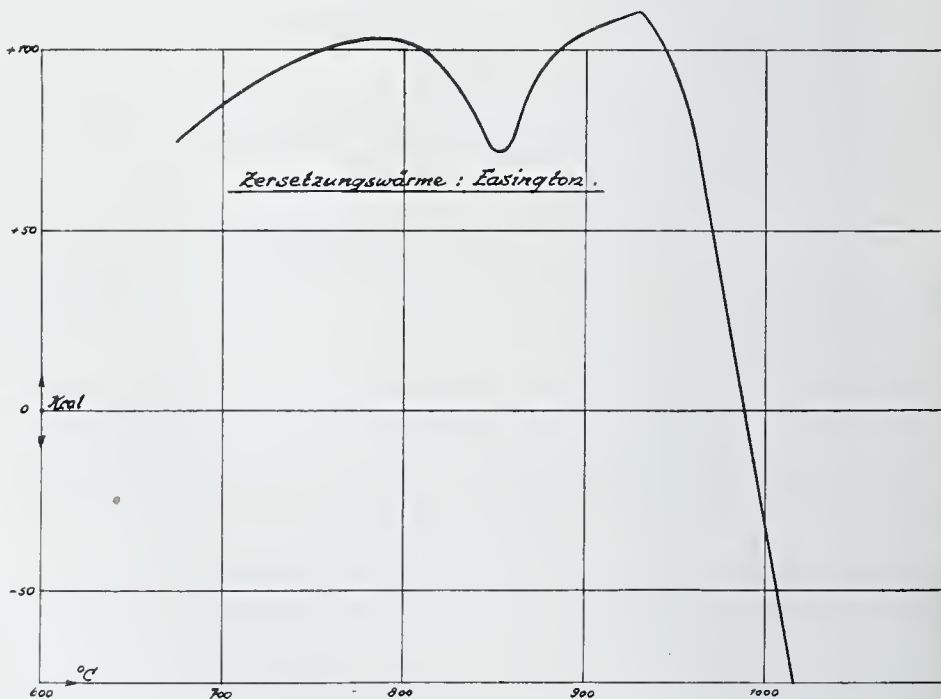


FIG. 13. DECOMPOSITION HEAT CURVE FOR EASINGTON COAL

*Zersetzungswärme* = heat of decomposition

value of about 150 kcal. per kilogram of air-dried coal; from that point the curve of the coking heat shows with increasing temperature a steeper slope than any other coal we have observed up to now; at 1000°C. the coking heat amounts to 330 kcal. and at 1050°C. it reaches the value of 560 kcal. Moreover the curve of coking heat shows two maxima, which point to reactions of considerable negative reaction heat at about 800° and 930°C.

The decomposition heats, Figure 13, are predominatingly positive up to about 930°C. and reach values up to plus 121 kcal. Beginning

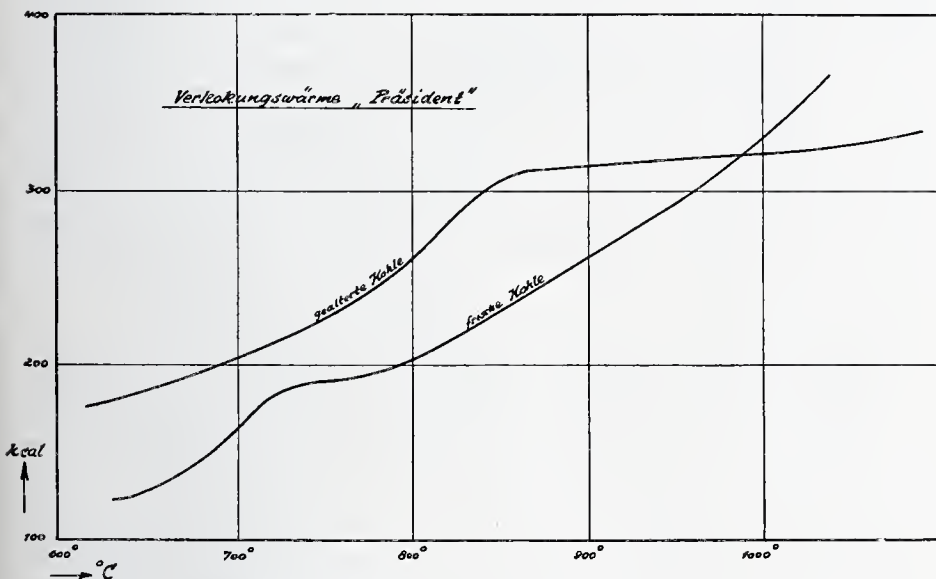


FIG. 14. COKING HEAT CURVES OF FRESHLY MINED AND OF STORED  
"PRESIDENT" (RUHR) COAL

*Verkokungswärme* = coking heat.

*gealterte Kohle* = aged coal.

*frische Kohle* = fresh coal.

at 930° the curve drops very abruptly and shows at 1000°C. a value of minus 25 kcal. and at 1025°C. minus 100 kcal. This strong endothermic character of this coal at high temperatures explains also its behavior in coke ovens.

It is of great interest to examine also the influence of storing upon the intensity of the coking and decomposition heat of a coal. It is generally known that a coal, which has been stored for a rather long time yields less gas and often less firm coke and that such a coal requires a larger fuel consumption in the coking process. These observations have been confirmed by the change found in the values

of the coking and decomposition heats. Figure 14 shows the curves of the coking heat of the same coal, first when coming directly from the mine and second after it has been stored for two years. The fresh coal has a lower coking heat than the sample which had been aged, but also the form of the curve has become quite different. This shows the influence of storing on the well-known "President" Ruhr coal.

The curves of the decomposition heats show the influence of aging of coals still more strikingly. The fresh coal has the highest heat of decomposition in the whole range of temperature up to  $1000^{\circ}\text{C}.$ , with an increasing storage time the endothermic reactions preponderate evidently more and more in the coking process and the exothermic reactions disappear more and more. The ingredients of coal thus undergo a change when stored, which shows itself in the disappearance of the exothermic reactions. It may be accepted that if the storage lasts a sufficient time, a final state results upon which a longer storage has no more influence; especial tests now in progress will clear up this point.

Also the moisture content of coal exerts a large influence upon the magnitude of the values of the coking heat. We have at first the impression that, knowing the coking heat of the air-dried coal, the heat requirement for the coking process could be calculated for every moisture content, considering the heat requirement for the evaporation of the moisture. That is not the case. The wet coal has, especially at higher temperatures, a much higher coking heat than results from the calculation. At the higher temperatures the water vapor reacts with the ingredients of the coal or of the coke in such a way, that an absorption of heat occurs, evidently due to the formation of water gas. We may explain this from the fact that the outer layers of the coal are already transformed into coke and have a proportionately higher temperature before the evaporation of the moisture in the interior of the coal has ended. The steam must pass through the exterior incandescent layers of the coal where a reaction occurs.

Figure 15 shows you the corresponding curves of the coking heat of the same coal, first in an air-dried state and then with 10.7 per cent of moisture. The wet coal shows in the range of temperature above about  $600^{\circ}\text{C}.$  an extraordinary increase of the coking heat.

These influences of aging and moisture found by us show that such investigations can be of value for large scale production only

if tests are made with samples of coal, which are fresh and in the same state as the coal used in actual operation.

Likewise the coking heats of coal mixtures are not always composed additively of the corresponding values of the components. Tests on this point are still going on.

However, the question imposes itself, whether it will not be possible to derive a rule for the determination of the coking heat by the way of calculation based upon other data of coal analysis. That is not the case up to now as you can readily see. The reactions of the

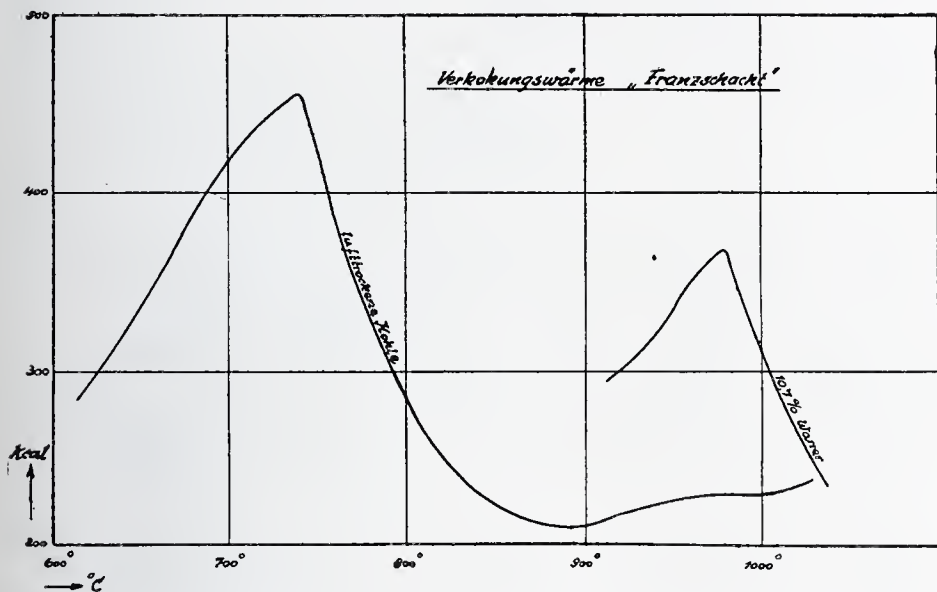


FIG. 15. COKING HEAT OF COAL, FIRST IN AIR-DRIED STATE AND THEN WITH 10.7 PER CENT MOISTURE

*Verkokungswärme* = coking heat.

*lufttrockene Kohle* = air-dried coal.

*Wasser* = water.

coking process depend upon the nature and the composition of the bitumen. We mean by the term bitumen the most varied substances with certain properties and it is sure that the composition of these substances is quite different in each coal and also in coals of the same origin. Therefore it cannot be expected that an even approximately valid rule is at all possible.

But there is an obvious connection between the coking heat and the decomposition heat of a coal, at least this connection holds good for the heat values of the coking process at 1000°C. In Figure 16

you will find brought together the normal coking heats at  $1000^{\circ}\text{C}$ . of 28 different kinds of coal from many different coal districts. You see that all these coals arrange themselves without constraint in a

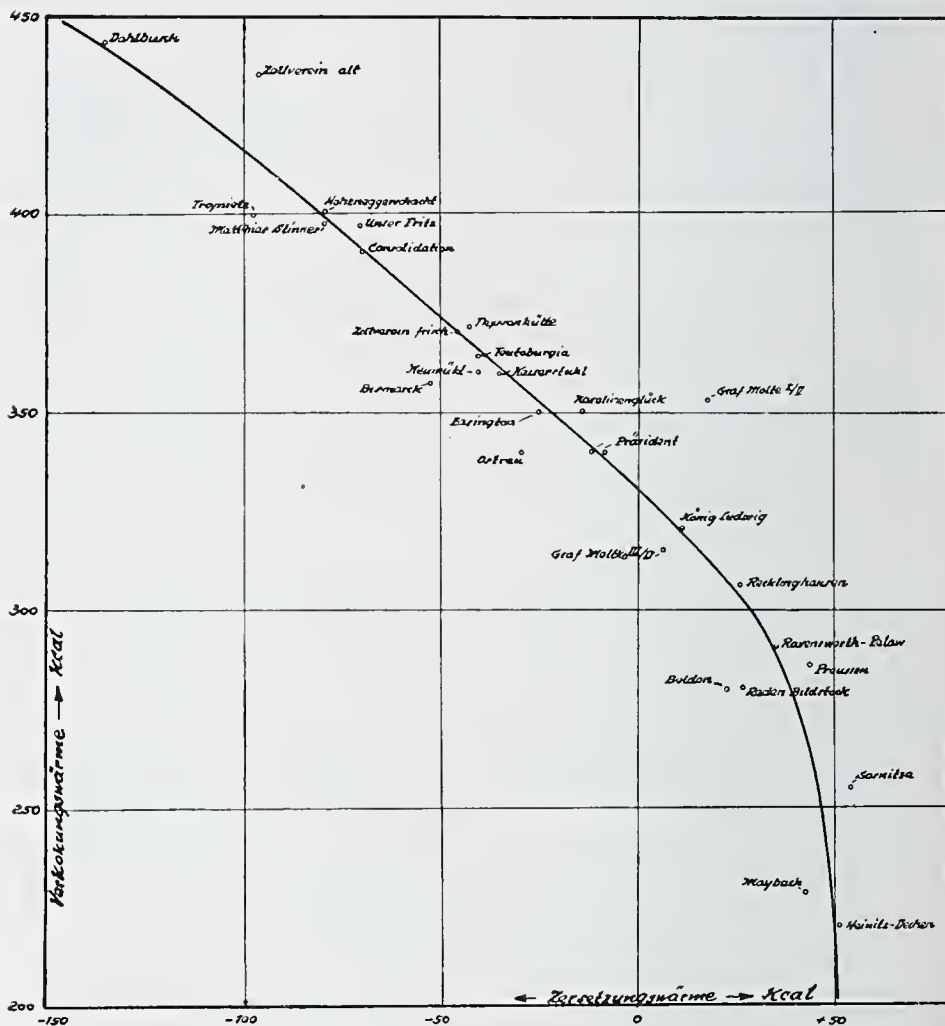


FIG. 16. COKING HEAT AT  $1000^{\circ}\text{C}$ . OF 28 DIFFERENT COALS

*Verkokungswärme* = coking heat.

*Zersetzungswärme* = decomposition heat.

*Zollverein alt* = old Zollverein.

*Zollverein frisch* = Fresh Zollverein.

curve. The ordinate is erected at the zero point of the abscissa and the values of the coking heat are marked upon it; to the right and the left of the ordinate the values of the decomposition heat are indicated upon the abscissa according as they are positive or negative. All

the coals arrange themselves in this manner that the coals with the highest positive heat of decomposition are on the one end of the curve and the coals with the highest negative values are on the other. The resulting curve cuts the ordinate in a point which corresponds to a coking heat of 325 kcal. per kilogram of pure coal (free of ash and moisture) of which the heat of decomposition is zero at 1000°C. The more positive the heats of decomposition are, the lower the coking heats lie below 325 kcal. and the more negative the heats of decomposition are the higher the coking heats lie above this number.

But the curve shows us still more. It has the practical significance, that we are able to derive by means of this curve the heat of decomposition of any coal, at least approximately, if we know the heat of coking at 1000°C.

We learn further from the curve that we must deal with very considerable negative heats of decomposition in the coking process, but that in the range of the positive heats of decomposition at 1000°C. we have to do with decomposition heats scarcely higher than plus 50 kcal. per kilogram of pure coal at 1000°C. You will ask me now whether these values of the coking heat, determined in the laboratory, may serve as a basis for the judgment of coals in coking plants. The solution of this problem was the practical aim of these investigations, and as you remember, we had planned to determine the net efficiency of coke ovens based upon the coking heat. The application of the laboratory results to practical coke oven operation gave at first however widely fluctuating values for the net efficiency of oven plants, ranging from 52 to 67 per cent. At first, the practical engineer was astonished that coals with a coking heat of about 200 kcal. showed in practice a coking time of only two hours less than coals with 300 and 350 kcal. per kilogram of coal. However we succeeded in explaining this apparent contradiction; it is caused by the different conductivity of heat of coal and coke which is quite different in swollen coke and in dense coke. The measurements of the conductivity of heat which we have made in the meantime enable us now to calculate with a sufficient accuracy for practical purposes the coking time of very different coals for all possible widths of chambers. Before I give you more details on this point, I should like to say a few words concerning the causes of the different net efficiencies found in practical operations.

The fuel consumption of a coke oven is composed of:

1. The heat requirement for the transformation from coal into coke, that is the product of the quantity of coal in kilogram and the coking heat per kilogram of coal.

2. The heat of the products of combustion leaving the recuperator or the regenerator.

3. The heat loss of the oven by conduction and radiation.

The heat of coking can be determined experimentally, as I have shown before; the heat loss in the combustion gases can be obtained from the amount of coke consumed, from the composition of the producer and combustion gases, from the water vapor content of the combustion gases, from the temperature of the gas upon leaving the oven, and from the mean specific heats referred to the waste gas temperature. It is more difficult to discover the loss of heat of the oven by heat conduction and radiation; but this value also can be determined with sufficient accuracy by experiments. Experiments still in progress have shown that in this manner the fuel consumption can be determined, and that the coking heat can serve as a basis for estimating it.

The types of ovens show great variations in reference to the heat losses by convection and radiation. These losses are greater than one usually supposes; they amount to 15 to 30 per cent and more of the total fuel consumed. They are least in the case of the coking oven with horizontal chambers and regeneration, that is, about 15 to 20 per cent; in case of gas works ovens they are greater; they differ depending upon the type of oven. Continuously operated ovens show the lowest losses; on the average in the gas works ovens the losses by convection and radiation fluctuate between 15 and 35 per cent. The heat losses due to the hot waste gases are smaller and more constant; lie between 15 and 20 per cent of the fuel consumed. Thus it is entirely possible to take the coking heat as a basis for the calculation of the fuel consumption and the net efficiency of coking ovens, and it is to be expected that this kind of estimate of the oven plant will contribute to reduce the heat losses of ovens by convection and radiation that are today, to some extent, quite large, to the smallest amount possible. There is still very profitable work to be done in the realm of oven construction and heat insulation.

On the other hand we are able to use the values of the coking heat for calculating the coking time of the different coals for different width of chambers, as I have already told you. For this we have

to know the heat conductivity of coal and coke at different temperatures and different degrees of distillation. We have also carried out such measurements and I can inform you concerning the first results by the aid of which the problem we have undertaken is solved in principle.

We<sup>9</sup> have measured in extensive experiments the heat conductivity of coal and coke in the range of temperature between 20° and 1000°C. according to the method of Heyn and Baur<sup>10</sup> and the calorimetric method of Görrens.

The method of Heyn and Baur is based on the fact that the heating up of the front surface of a certain volume of the material to be tested is measured as a function of time; in the middle axis of this front surface is built in at a given distance a second thermo-element, the rise of temperature of which is also registered depending upon the time. With the aid of calculated temperature time-curves the heat conductivity of a material can be calculated from these measured temperature-time curves by a complicated mode of calculation.

The method of Görrens determines the heat conductivity in a calorimetric way. One of the surfaces of the material to be investigated is brought into contact with a constant source of heat, while at the opposite surface the transmitted quantity of heat is measured calorimetrically. The heat conductivity for any temperature range can be determined from the quantity of heat transmitted in a unit of time, the temperature difference, the thickness of the material to be investigated, and the surface of the calorimeter in contact with the material.

For various reasons, which I cannot explain here in detail, the method of Heyn and Baur is better suited for measurements with coal and coke, than that of Görrens.

We have measured the heat conductivity with coal of different grades of fineness and with a compact piece, as well as with coke of different grades of fineness and with compact pieces of different stages of coking.

We have found in accordance with former measurements of Taylor, Forbes, Cellior, Neumann and Hecht, that coal itself possesses an exceedingly small heat conductivity, which amounts to only the

<sup>9</sup> E. Terres u. H. Heidenreich, not yet published.

E. Terres—Sander, not yet published.

<sup>10</sup> *Mitteilungen aus dem Material prüfungsamt zu Berlin-Lichterfeld-West*, 1914, Heft 2 u. 3.

eighth or the sixth part of that of firebrick. If we express the heat conductivity value as gram Calories per square centimeter with a thickness of 1 cm. and a temperature difference of  $1^{\circ}\text{C}$ ., then firebrick gives the mean value of 0.0024 while coal has only the value of 0.0003

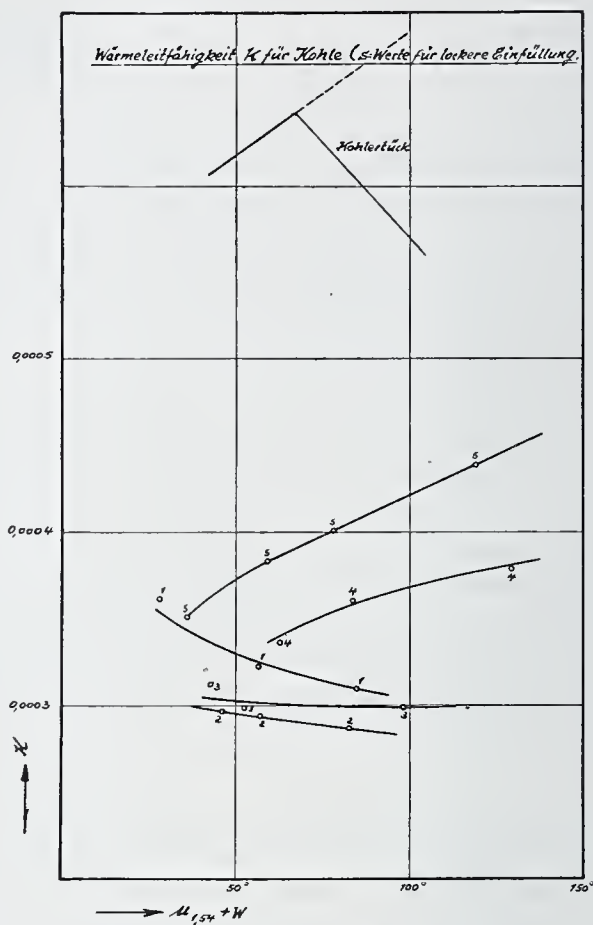


FIG. 17. HEAT CONDUCTIVITY BETWEEN  $20^{\circ}$  AND  $150^{\circ}\text{C}$ . FOR GRANULAR SIZES AND FOR COMPACT LUMP OF COAL

Wärmeleitfähigkeit  $K$  für Kohle (S-Werte für lockere Einfüllung) = heat conductivity  $K$  for coal (S-values for loose filler.)  
 Kohlestück = piece of coal.

to 0.0004. The granular size of the material has a great influence and Figure 17 shows you, for some sizes and for a compact piece of coal, the heat conductivity in the range of temperature between  $20^{\circ}$  to about  $150^{\circ}\text{C}$ . You see here the measured values for the different sizes of the grain from 0 to 1, 1 to 2, 2 to 3, 3 to 4, and 4 to 5 mm. and

for a compact piece. The break in the curve for a solid piece can be explained by the fact that at higher temperatures changes take place in the coal and the suppositions underlying the method of Heyn and Baur are no longer fulfilled.

Degasified coke gives considerably higher values. The large influence of the size of the grains can also be easily recognized here in so far as the larger grain results in higher values. You see in the curves,

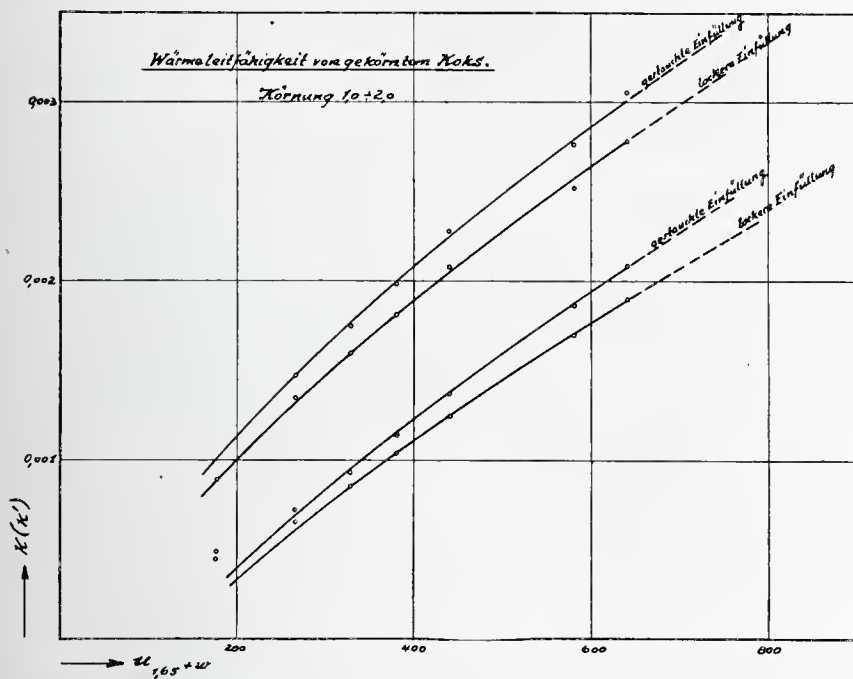


FIG. 18. HEAT CONDUCTIVITY OF GRANULATED COKE

Wärmeleitfähigkeit von gekörntem Koks = heat conductivity of granulated coke.

Körnung = granulation 1 ÷ 2.

gestauchte Einfüllung = tamped filling.

lockere Einfüllung = loose filling.

Figure 18, that coke can reach at higher temperatures higher heat conductivity values than firebrick.

For our purposes, we need the heat conductivity for the continuous transition from coal of 20° into coke of 1000°C. These values have been determined with compact pieces of coke, which were obtained at different coking temperatures. In this way, corresponding values for the continuous transition of coal into coke are obtained. The values differ according to the porosity of the produced coke. I have put together in Figure 19 three curves with the mean values of heat

conductivity between 0° to 1000°C. for the continuous transformation of coal into coke, of which the lower curve refers to a puffed coke, as it is produced from Saar coal; the middle curve refers to a gas coke of an average hardness and density; and the upper curve refers to a dense blast furnace coke. The puffed coke has the smallest, and the densest coke the highest values of heat conductivity. The exact

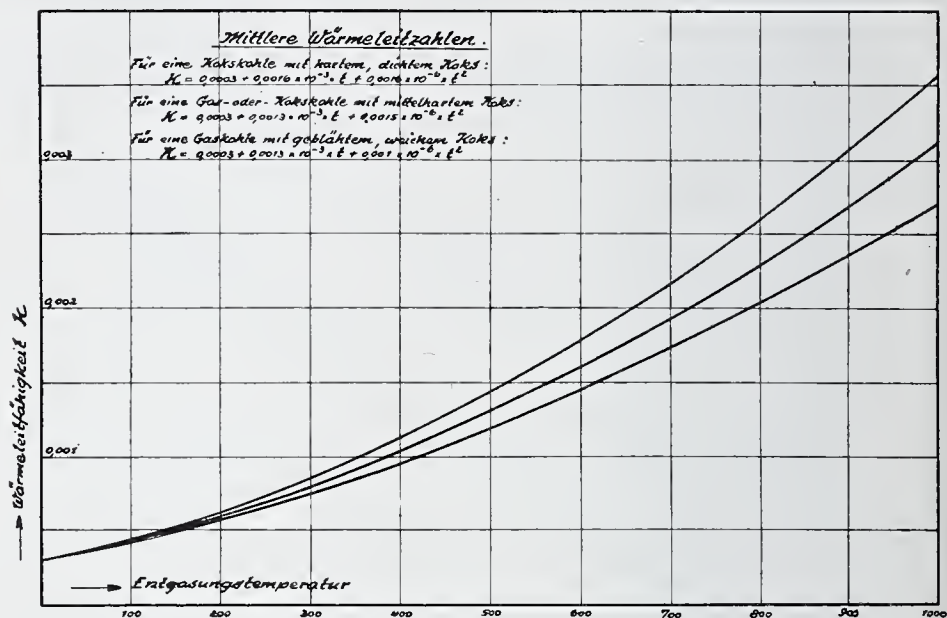


FIG. 19. AVERAGE HEAT CONDUCTIVITY FOR THREE COALS

*Mittlere Wärmeleitzahlen* = average heat conductivity numbers.

*Für eine Kokskohle mit hartem, dichtem Koks* = for a coking coal with hard, dense coke.

*Für eine Gas- oder Kokskohle mit mittelhartem Koks* = for a gas coal or a coking coal with coke of average hardness.

*Für eine Gaskohle mit geblähtem, weichem Koks* = for a gas coal with puffed soft coke.

*Wärmeleitfähigkeit* = heat conductivity.

*Entgasungstemperatur* = distillation temperature.

values can be interpolated for each kind of coke by measuring the coke porosity, generally, however, one of these three curves will be sufficient for a numerical estimate. The separate values are only tentative and are claimed to be no more than an approximation. Investigations still in progress will give in a short time definite values.

For making calculations we require an equation for each of these three curves, which expresses the variation of the heat conductivity with growing coking temperature.

I have tried to derive empirical formulas which represent the curves in a satisfactory manner. The mean coefficients of heat conductivity can be calculated by the following formulas:

For the coke coal, which gives a coke of high density:

$$k = 0.0003 + 0.0016 \times 10^{-3}t + 0.0016 \times 10^{-6}t^2$$

For the gascoals, which give a coke of average density:

$$k = 0.0003 + 0.0013 \times 10^{-3}t + 0.0015 \times 10^{-6}t^2$$

And for gascoals which give spongy coke:

$$k = 0.0003 + 0.0013 \times 10^{-3}t + 0.001 \times 10^{-6}t^2$$

The difference in the coefficient of heat conductivity is the reason why coals with low coking heat values reach approximately the same or only slightly different coking times as coals with high values of coking heat. The ability to calculate the coking times is required in order to derive from the values of the coking heat, the yield of a coke oven and the actual fuel consumption.

If we base the calculation on 1 square meter of the chamber wall, 24 cm. as half of the chamber width, and a weight of a cubic meter of coal of 0.8 ton, we obtain the following equation:

The coking time in hours  
at 1000°C. coking temper- =  
ature

$$\frac{\text{Coking heat in kcal./kgm.} \times \text{weight of the coal} \times 1000 \times \frac{1}{2} \text{ chamber width}}{(0.0003 + 0.0013 \times 10^{-3} \times 1000 + 0.0015 \times 10^{-6} 1000^2) \times 10000 \times \Delta t \times 3600}$$

\* In a volume formed by one square meter of chamber wall and half the chamber width.

Example: Let the coking heat be 325 kcal. per kilogram of air-dried coal. The weight of the volume of coal per 1 square meter of chamber wall having half of the chamber width for its thickness is equal to 192 kgm. The coking time is found to be:

$$\frac{325 \times 192 \times 1000 \times 24}{0.0031 \times 10000 \times 500 \times 3600} = 26.84 \text{ hours}$$

Thus according to the above formula Saar coal with the small coking heat of 240 kcal. per kilogram gives with a chamber width of

480 mm. on account of its lower heat conductivity at  $1000^{\circ}\text{C}.$ , a coking time of 22.8 hours; and a coking coal with 400 kcal. per kilogram of air-dried coal gives for the same width of the chambers a coking time of 28.3 hours. These are values, which agree sufficiently with practical experience.

In the same way there can be calculated the coking time for the three types of coal for any width of the coking chamber and any coking temperature: for instance, for coking at low temperatures. We are able to determine by calculation the width of a coking chamber for a coking time of 12 hours or for any other coking time; and in the same way we can estimate the fuel consumption required, if we know the heat losses of the oven by convection and radiation. Also it is possible to calculate the coking time and the fuel consumption for greater temperature potentials than are now usual in coke ovens.

All these are data, which are of great importance for the design of ovens and which could be determined up to the present time only by costly large-scale experiments. Thus a long-standing want of the industries of coking and oven design has been met.

From the smallness of the coefficients of heat conductivity of coal and coke which are partly smaller, partly equal or only a little higher, than those of firebrick and silica brick, it is evident that even if we could find a building material for the walls of the oven chambers with a higher heat conductivity, it would not be possible to decrease essentially the time of coking, since coal and coke themselves offer the greater resistance to the transmission of the heat.

From this you will see that the measurements made by us can be of a great importance in many different respects, and I hope, that, I have been able to give you a sufficiently clear idea of heat expenditure in coking in spite of the complex nature of the subject.

## THE DRY QUENCHING OF COKE

By D. W. WILSON

*Vice-President, Dry Quenching Equipment Corporation, New York*

All methods of high temperature carbonization of coal, except the continuous vertical retort, involve as a necessary part of operation, the discharge of coke from the processing equipment at a temperature of from 1750°F. to possibly 2150°F. It has long been recognized that the sensible heat contained in the coke due to this high temperature represents a large percentage of the fuel requirement of the coking process. This is strikingly evident to all who are familiar with the hot coke as produced at coke oven plants and with the immense clouds of vapors (representing wasted energy) produced during wet quenching.

To get a proper perspective upon this matter of wasted energy, it is worth while to examine briefly the history of coke making, particularly in the United States. The earliest large scale production of coke came from beehive ovens. These made no attempt at any conservation of coal gas, ammonia, tar, or oils, but resulted in the production of coke only, from the raw bituminous coal. This tremendous waste was followed by development of the recuperative coke oven which represented an important advance in coal processing since it conserved the ammonia, tar, and to some extent, the oils and the coal gas. However, in the use of fuel for underfiring, this design of oven was extremely wasteful due to very high waste gas temperatures. Consequently there followed, in an effort to conserve to the utmost the heat in the coal gas, the introduction of the regenerative oven in its various modifications. Each of these steps in coke oven development has been caused by the increasing economic pressure to conserve both materials and energy. It should also be noted that each of these steps has involved an increased initial capital expenditure which, however, has been amply repaid by the resulting conservation. The dry quenching of coke represents one further step in energy conservation since it aims at the conversion of the sensible heat in the hot coke (now entirely wasted) into some form of useful energy.

Let us now examine specifically, the potential benefits involved in saving this heat in the coke. Careful investigations have established

the average specific heat of coke from 1800°F. to usual atmospheric temperatures to be about 0.36.<sup>1</sup> This figure varies somewhat with the properties of the particular coke being considered, but this may safely be used as an average. If now the fuel gas (as coke oven gas) be taken at 4000 cubic feet of 540 B.t.u. gas per ton of coal carbonized, by simple calculation it is found that the sensible heat in the coke on the basis described represents 40 per cent of the heat in the gas required for carbonization. In other words, if it be assumed that coke as produced averages 1800°F. temperature, the saving in heat resulting from putting all this energy into useful form would be 40 per cent of the total gas required as fuel. In 1926, in the United States alone, about 44,000,000 tons of by-product coke were produced. If this coke be assumed to have been made entirely with the use of coke oven gas as fuel and if this gas be valued at 25 cents per M. cubic feet, the saving resulting from conservation of all the sensible heat in the coke, in the form of energy having equivalent value to that of coke oven gas, would amount to \$25,000,000. If all the heat in this coke be conserved and the saving, therefore resulting, be referred to producer fuel, (at \$5 per ton and taking 260 pounds per ton of coal carbonized), the total annual saving amounts to about \$11,000,000. If now, instead of considering total theoretical saving either in terms of coal gas or of producer gas, this be taken in the form of steam and based upon actual average production figures, we find that 44,000,000,000 pounds of steam would actually have been produced from this coke. If a value of 25 cents per M. pounds be given to this steam, it is then found that the actual total gross saving which could have been effected would amount to \$11,000,000.

From these figures it would seem that the best method of conservation of this heat would be to utilize it so that it should result in a reduction of gas required for underfiring. This is in accord with the general principle regarding waste heat recovery that where possible it is most economical to reclaim this energy so that it results directly in a reduction of the fuel required by the apparatus furnishing the waste heat. However, in the case of hot coke resulting from coke oven operations, there seems no way in which the heat of the coke can be made directly applicable to the reduction of the coke oven fuel since the waste gases, by means of the incoming combustion

<sup>1</sup> "Studien über die spezifische Wärme von Koks und einigen Kohlen, stoffmodifikationen," by Paul Debrunner. *Monats-Bulletin des Schweizer-Vereins von Gas- und Wasserfachmannern*, Jahrgang, 1924.

air, are already reduced in temperature to from 500° to 700°F.; consequently, other means of conserving this energy must be utilized.

The production of steam represents a suitable and convenient means for the use of this heat. To be sure steam represents a lower priced form of energy than coke oven gas, but in this case as has been outlined, heat recovery in the form of coke oven gas is not practicable. The problem then is that of some type of waste heat boiler by means of which the sensible heat of the coke may be converted into steam. It should be noted here that this type of waste heat recovery differs radically from the usual installation. Ordinarily, as in the cases of open hearths, heating furnaces, kilns, water gas machines, and the like, the stack gases from the main producing unit pass through the waste heat boiler. Consequently draft conditions and therefore combustion of the furnace proper may be seriously affected by operation of the waste heat unit. This means that operating conditions as to capacity and sometimes other factors may be deeply influenced by the waste heat boiler installation. In coke dry quenching, these considerations do not apply since the waste heat recovery deals with the coke after it is discharged from the ovens, and therefore this process in these respects is wholly independent of the coke oven operations.

Dry quenching then consists in devising a simple, practical, and economical means of transferring the sensible heat of the hot coke into steam. Various schemes have been proposed, and many patents have been issued. In some plans, advantage is taken of the radiant heat of the coke, while in others, the heat is transferred first by passing hot gas through the coke, then by passage of this hot gas through boiler tubes converting it into steam. Some schemes transfer heat from the coke to steam by a combination of radiation and hot gases. Some methods involve movement of the coke, while others do not. Several technical papers have been presented covering the different processes and the results obtained from them. Perhaps the most valuable among these are the ones by Leather,<sup>2</sup> by Beebee,<sup>3</sup> and by

<sup>2</sup> "Coke Cooling," by John P. Leather, *Gas Journal* (English), June 22, 1927.

<sup>3</sup> "Experiences with Dry Quenching Coke Plant at Rochester, N. Y.," by A. M. Beebee, *Gas Age-Record*, March, 1927. "Advantages and Disadvantages of Dry Quenching of Coke," by A. M. Beebee, *Gas Journal of Canada*, August, 1927. "Economies of Dry Quenching Coke by the Sulzer Process,"

Sissingh.<sup>4</sup> The process which has so far found greatest commercial favor is that devised by Sulzer Bros., of Winterthur, Switzerland. Fundamentally, this consists in passing a stream of inert gases upward through a considerable body of hot coke, the hot gases then passing through or around boiler tubes, thence to a fan by means of which they are again returned to the coke. This scheme involves elevating the hot coke if the plant is placed above yard grade, or elevating the cold coke if the plant be placed below ground elevation. It has the important advantage of counterflow of coke and circulating

TABLE I  
HEAT BALANCE—DRY QUENCHER  
Basis 1 net ton dry coke—32 °F.

	BRITISH THERMOL UNITS	PER CENT TOTAL INPUT
<i>Input:</i>		
Sensible heat coke.....	1,288,000	79.0
Heat feed water.....	153,000	9.4
Combustion of coke volatile matter.....	190,000	11.6
Total.....	1,631,000	100.0
<i>Output:</i>		
Steam.....	1,217,000	74.6
Sensible heat of coke.....	325,000	19.9
Radiation and convection.....	49,000	3.0
Unaccounted.....	40,000	2.5
Total.....	1,631,000	100.0

gases. Inasmuch as this process is the only one to have attained commercial success in this country, discussion in this paper will be confined to results obtained from it.

A consideration of dry quenching may conveniently be classified into two divisions: First, its technical and operating aspects and second, its economic aspects. First, considering the technical side of the question, we may divide it into two classifications: First, the heat efficiency and steam production and second, coke qualities resulting from the process. The most comprehensive way of studying the heat economy is by means of the heat balance. In Table I

by A. M. Beebee, Paper at A.S.M.E. Fuels Division Meeting, St. Louis, October 10-13, 1927.

<sup>4</sup> "Trockene Koksloschung auf dem Gaswerk zu Rotterdam-Keilehaven," by M. C. Sissingh, *Das Gas und Wasserfach*, December 22, 1923.

is given a summarized heat balance showing the performance of the dry quenching installation located at Rochester, New York.

It is of interest to know the general operating conditions as to gas temperatures, coke temperatures, steam production, and similar information and therefore Table II is given to summarize these.

TABLE II

OPERATING DATA—PLANT OPERATING AT 540 TONS COKE DAILY

*Coke temperature:*

Inlet.....	1780°F. Heat content—634 B.t.u./pound
Outlet.....	600°F. Heat content—160 B.t.u./pound

*Steam:*

Pressure.....	140 pounds/square inch
Quantity.....	1005 pounds/ton coke
Temperature.....	361°F.

*Feedwater:*

Temperature.....	182°F.
------------------	--------

*Circulating gases:*

Temperature	
Inlet boiler.....	{ Maximum, 1300 Minimum, 980 Average, 1140 °F.
Outlet boiler.....	360°F.
Volume.....	20,000 cubic feet/minute at 360°F.
Pressures.....	{ Fan inlet, -2.8 inches water Fan outlet, +4.8 inches water
Analysis (entering coke container)..	{ CO <sub>2</sub> 10.0 per cent O <sub>2</sub> 0.1 per cent CO 6.0 per cent H <sub>2</sub> 6.0 per cent N <sub>2</sub> 77.9 per cent

In Table I, the heat obtained by combustion of the volatile matter of the coke is obtained from a knowledge of the reduction in volatile in the coke resulting from dry quenching. Many tests at Rochester have shown this to average 0.6 per cent. This devolatilization occurs mainly in the coke from the ends and top of the oven where there is some tendency toward undercoking. Consequently, this reduction in volatile produces a more uniform coke and in this way is a considerable benefit. While it is not possible to determine exactly how much heat is contributed from this source, taking the reduction in volatile

as 0.60 per cent and the heating value of it as 16,000 B.t.u. per pound, we arrive at the figure of 190,000 B.t.u. per ton of coke as given in Table I. Admittedly the figure of 16,000 B.t.u. per pound is an estimate only, but remembering that carbon has a heating value of 14,500 B.t.u. per pound, and that this volatile matter contains considerable hydrogen, it is entirely reasonable to expect its heating value to exceed that of carbon. The point might be raised that if air be available for combustion of volatile matter, then coke combustion is probable. In answer to this, we may say, that air for combustion of this volatile enters the dry quenching system at the top of the coke container, and therefore just previous to the entrance of the gases to the boiler. Observation shows that the combustion occurs only when the charging cover is open for admission of coke, and that this burning takes place almost entirely within the dry quencher and not, as might be thought, into the air above the charging opening. Furthermore, all the oxygen in this air is consumed before the gases leave the boiler, and therefore no coke combustion can possibly occur. Repeated gas analyses have shown that, at the point of entrance to the coke, the oxygen content is negligible and that the gases, due to the percentages of carbon monoxide and hydrogen, should be considered reducing rather than oxidizing. In Table II is given a gas analysis showing its composition at the point of entrance to the coke.

Radiation and convection heat losses were determined directly by means of surface temperatures and exposed areas. It is appreciated that such a procedure may be subject to error, but it should be realized that even a large percentage error in this item affects the heat balance only very slightly.

The steam produced was measured with a standard Bailey steam meter, which, however, was very carefully checked against actual tank measurements of the water used by the boilers during periods when there was no blowdown. The dry coke produced is taken as 69 per cent of the dry coal charged to the ovens. This is in accord with earlier tests made at the Rochester plant and conforms to other operating experience over long periods of time.

One important consideration in dry quenching is the question of coke dust. This is a twofold problem: First, the circulating gases carry with them fine coke which necessitates proper provisions that this shall not interfere with the proper functioning of the plant. In order to provide for this, dust chambers are installed in which gas velocities

are reduced in order that the fine solid material may separate. Efforts in this direction have been entirely successful and no difficulty is experienced on account of dust interferences to gas flow. The second problem with regard to coke dust depends upon the fact that absolutely dry coke, such as may result from this type of quenching, is extremely dusty, rendering working conditions difficult, and in the case of domestic coke, giving rise to customers' complaints. Under many conditions, absolutely dry coke will be sufficiently desirable to offset the dust disadvantage; however, it is entirely practicable, and in many cases, common practice, to sprinkle the coke as it issues from the dry quencher with a small and controlled amount of water, thereby eliminating any coke dust. In using water in this way, it is not necessary to add a measurable percentage of moisture to the coke unless this be desired. It is entirely possible to get away from coke dust production by the use of water, and at the same time, the moisture percentage in the large coke will not be measurable, and in the coke breeze will not exceed 2 to 3 per cent. This may be contrasted with coke breeze moisture percentages from ordinary wet quenching operations of from 12 to 18 per cent. It is desired to emphasize that the use of dry quenching permits, if desired, the production of an absolutely dry coke, and that in any event, the moisture content of the coke may be held entirely uniform at any desired figure. Low, controllable, and uniform coke moisture is a distinct advantage and should be contrasted with the variable moisture content from large to small coke, and often from one part of the quenching car to another which necessarily results from wet quenching.

Another operating advantage—in most plants—enjoyed by dry quenching, is the elimination of the quenching water. These quenching vapors are corrosive in nature, necessitating considerable plant steel work maintenance, and they also carry with them a considerable amount of fine coke dust which is distributed widely over the surrounding territory. For coke ovens located near business or residential sections, this may be an extremely important advantage resulting from dry quenching. In some situations also, the water from wet quenching becomes a source of maintenance in cold weather due to freezing troubles with conveyors and auxiliary machinery.

Turning now to the second technical aspect of dry quenching, that is, the resultant coke qualities, we find several interesting considera-

tions: first, as to the effect on coke structure, European experience has indicated that the result of suddenly spraying water upon the hot coke was weakness of structure due to sudden stresses established in the coke piece by rapid contraction. American experience, however, seems not to have borne out this idea. An excellent discussion of this point is given in a paper by Beebee, published in *Gas Age-Record*, March 19, 1927. Quoting from this paper which is based upon very careful tests, we find the following: "The coke structure of dry quenched coke is apparently not stronger fundamentally than wet quenched coke. This was considerable of a surprise to us, but we have such a volume of convincing data on this point, all of which are surprisingly consistent, that apparently there is no doubt of it." European results are directly opposed to this, indicating under their conditions splitting and breaking of coke when wet quenched. A possible explanation of these divergent conclusions may lie in differing methods of wet quenching. There is evidence to show that excessive water in wet quenching does shatter the coke pieces while this does not seem to be true if the minimum quantity of quenching water be used. This may be due to excessive water cooling the coke by actual contact between coke and liquid water, while a minimum use of water permits most of the cooling to be done by steam (probably considerably superheated). In accordance with this explanation, excessive quenching water would cause large, sudden temperature changes in the cooling of the coke, while the use of the minimum water would permit a relatively much more gradual cooling.

Another important consideration lies in the fact that in the wet quenching operation there is a considerable tendency for wet breeze to cling to larger pieces of coke. This fine coke is not removed during the screening operation, but will separate from the large coke later as the mass dries out. In the case of domestic coke, this is often the cause of complaints on the score of dirty coke. Definite experience has borne out this point that cleaner coke may be prepared for the domestic trade if the dry quenching process is used.

Another point of importance is with regard to coke breakage due to dry quenching. As may be observed from the description already given, the dry quenching process involves more handling and more movement of coke than is the case with wet quenching. Experience in the United States has very positively shown that the result of this additional handling is that at the coke oven plant itself, dry quenched coke is smaller in size than wet quenched, although this reduction in size may, if desired, be made small by the most suitable design of coke

handling apparatus. On the other hand, this smaller sized coke is more uniform in size, physically stronger, and consequently much more resistant to further handling.

Let us turn now to the various uses to which coke is put and examine each of these in the light of the properties just described and also with respect to such experience as is available. Principally, coke is used in the following ways:

- (1) As water gas fuel.
- (2) As producer fuel.
- (3) As blast furnace fuel.
- (4) As domestic fuel.
- (5) For foundries.
- (6) In industrial furnaces.
- (7) In boilers.

Careful comparisons have been made at Rochester, N. Y., between dry and wet quenched coke for use in water gas machines. Several tests have shown that about 5 per cent better fuel economy, compared on the dry basis, is obtained when dry quenched fuel is used. It is difficult to give a satisfactory theoretical explanation of this since it is quite impossible to account for the better performance on the basis of the heat required to drive off the higher moisture content of the wet quenched fuel. The statement has been made that the absence of moisture permits an extension of the reducing zone in the water gas machine and consequent fuel economy. It may be that this explanation is correct, but sufficient experimental evidence is not yet available to enable a conclusion. It is possible that the better screening, the more uniform size, and the physically stronger coke permits a more uniform and regular operation of the water gas machine, and that this accounts for the better results obtained. Whatever the explanation may be, the experimental evidence seems entirely convincing that in the production of carburetted water gas about 5 per cent better fuel economy is obtained using dry quenched coke.

Experiences involving the use of dry quenched coke as producer fuel show also definite economies amounting to a lower fuel consumption by 10 pounds of carbon per ton of coal carbonized when dry quenched coke is used. This then represents about 5 per cent better economy. Here again, no satisfactory explanation seems available although there are several possibilities. The lower percentage of moisture in the dry quenched producer fuel is not enough to explain the economy effected. It is in this case, however, highly

possible that the much more uniform moisture content of the dry quenched fuel has an important bearing upon its use. In this particular case, this may readily be very important, as producer fuel may consist of all sizes of coke from possibly  $\frac{7}{8}$ -inch diameter down to dust. Now in ordinary wet quenching, the moisture percentages of the various sizes of coke, particularly in these smaller ranges, vary widely. The resistance, therefore, of the fuel bed to the passage of gases would be much more variable in the case of wet quenched coke; consequently, gas channeling would occur to a greater extent and the producer operation be highly irregular. Experience has actually shown that something of this sort exists, because if dry quenched fuel be used, smaller sizes of coke can be utilized and actually with better producer working conditions. This means, of course, that inferior fuel, with a higher ash content, can be successfully used in producers if dry quenched fuel be used.

For blast furnace fuel, unfortunately no American experience is available. However, several factors have an important bearing upon this. The coke moisture from the dry quenching operation may, if desired, be held at zero. Usually, however, some water will be used. In any event, the resulting moisture in the coke will be very low, and always will be practically uniform. It is believed that this uniformity of moisture should be of prime importance in blast furnace operations. Furthermore, the uniform size and greater physical strength of the coke should lead to better furnace operation and lower fuel requirements. The economies effected in water gas machines and in producers would lead to the conclusion that some similar blast furnace economy should be inevitable. In the blast furnace, as in these other coke consuming machines, the problem with regard to carbon is, first, its conversion to dioxide, then to carbon monoxide, followed by its partial reoxidation. This similarity in carbon utilization in the blast furnace and in producer and water gas machines, considered in the light of established economies in the latter two types of equipment, certainly gives strong indication that blast furnace fuel economy would result from dry quenched coke. Furthermore, there are two European plants using dry quenched coke as blast furnace fuel, and each of these reports an economy, due to this cause, of from 2 to 5 per cent. It is fully realized that American conditions as to blast furnace operations and raw materials are widely different from those prevailing in Europe, and therefore results obtained there cannot be regarded as conclusive evidence that

similar results would be obtained here. Nevertheless, consideration of the better fuel results in producers and water gas machines and the stronger, more uniform coke indicates strongly that important blast furnace economies will result from the use of dry quenched coke.

Considered from the standpoint of domestic fuel, there are important points in favor of dry quenching. An advantage which has definitely proven itself is that better screening is possible, and therefore a cleaner coke, freer from breeze, may be supplied domestic customers. Precautions must be taken to avoid supplying to the domestic trade coke which is so dry as to be dusty and this is true whether wet or dry quenching be practiced. This need not occur in dry quenching provided adequate water be added to the coke after screening and before supplying to the customer, thus retaining the advantage of the better preparation of the dry coke and eliminating wet breeze adhering to the larger coke. Statements have been made that moisture cannot be added to cold coke so that the latter will retain it and therefore keep down dust as well as can be done during wet quenching. Experiments made at Rochester have, however, shown that there is no difference in the capacity of coke to add moisture and in its retention of it, whether wet quenching or dry quenching be practiced. It would seem then that the use of dry quenching with regard to domestic coke has no disadvantage, provided sufficient moisture be added to the coke to prevent dust difficulties, and that it offers the important advantage that a cleaner coke freer from breeze may be supplied.

For use in foundries, in case especially large coke be essential for a particular purpose, it is probable that the dry quenching process would be at a disadvantage as it certainly tends to produce coke smaller in size than the wet quenched product. However, it would seem that, for most cases, dry quenched coke would offer advantages in that its moisture content should be less, and that it would be more uniform in this respect. Also the greater physical resistance of the coke to handling should be of great assistance to the foundryman, since the coke as delivered to the foundry would be more resistant to degradation and of a more uniform size.

With respect to use in industrial furnaces, little can be said except what has already been given. It is particularly difficult to give anything of value here, because requirements for industrial furnaces differ so widely from one case to another. However, it would seem there would be an advantage in having a stronger, cleaner coke with low uniform moisture content.

For use in boilers, ordinarily only breeze and the smaller sizes of coke find an outlet. Coke breeze from dry quenching will usually contain not more than 3 per cent moisture. The advantage which this product has over the wet quenched is apparent when one recalls that ordinarily wet quenched breeze contains from 12 to 18 per cent moisture, all of which requires heat to evaporate. Furthermore, the

TABLE III  
ECONOMIC SET-UP—PLANT CAPACITY—3300 NET TONS COKE DAILY  
All figures based on one year's operation

*Steam produced:*

840 pounds per ton above requirements of condensing turbines driving circulating gas fans.

$$840 \times 3300 \times 350 = 970,000,000 \text{ pounds/year.}$$

*Expenses:*

*Labor*

One man per shift @ 50 cents..... \$4,400

*Maintenance* (Credit reduced maintenance on hot car and no quenching water)

1.5 cents/ton more than above credits

$$0.015 \times 3300 \times 350 \dots\dots\dots 17,400$$

*Power:*

Hoist— $0.4 \times 0.01 \times 3300 \times 350 \dots\dots\dots 4,600$

Water— $0.800 \times 0.005 \times 60 \times 24 \times 350 \dots\dots\dots 2,000$

\$28,400

Cost of steam/M. pounds (exclusive of fixed charges)..... \$0.0293

*Fixed charges:*

$0.16 \times \$525,000 \dots\dots\dots \$83,900$

Cost of steam/M. pounds (fixed charges)..... \$0.0865

Total cost of steam..... \$0.1158

use of heat for this evaporation reduces furnace temperatures, and thereby impairs heat transfer from the combustion zone to the boiler tubes.

Turning now to the economic side of dry quenching, important advances in this respect have been made in the last few months. One of the chief costs of dry quenching has been the fixed charges on the necessary investment. Recent tests at Rochester, New York, have shown that by slight modifications of the apparatus very great increases in capacity are possible. It is proposed to give here the costs and the revenues from steam only, to be expected, based on

recent experience, in a plant handling in one unit 3300 net tons of coke daily. Additional revenue will be obtained from the higher quality of the coke, as experience cited earlier in this paper demonstrates, but this is so dependent upon local conditions that it is not attempted to include it. It is of interest to note that the ground area required by this plant is about 60 feet by 60 feet and that it may be located anywhere along the quenching track. These figures are summarized in Table III.

#### STEAM PRODUCED

Based on 1850°F. coke as pushed and with an ash content of 9 or 10 per cent and volatile of about 1 per cent, a total steam production of 950 pounds per ton of coke may conservatively be expected. Reference to Table II shows that at Rochester slightly more than 1000 pounds per ton of coke are actually made. In Table III, it is assumed that the circulating gas fans would be driven by condensing steam turbines. If electric power be sufficiently cheap, this of course would not be done. As will be shown below, about 110 pounds of steam per ton of coke will be required to drive the turbines, leaving, therefore, 840 pounds per ton above turbine requirements.

To allow for boiler inspection and plant maintenance, it is assumed that there will be 350 days operation per year. This is a conservative estimate, as it should be possible to have the plant out of operation only one week per year.

#### EXPENSES—LABOR

Experience has shown that one operator per shift is sufficient to take care of a dry quenching plant of this size. This is taken at 50 cents per hour as given in Table III.

#### MAINTENANCE

Experience at Rochester has shown that due to the absence of water and rapid heating and cooling, maintenance of the hot car is greatly reduced; also for many plants due to location of the dry quenching equipment, less travel of the quenching car will be necessary. Furthermore, the quenching car is required only long enough to dump its load into the bucket of the coke elevating equipment. For this reason more ovens may be handled per day per quenching

car. In a large plant, this would probably result in the use of fewer quenching cars. Also no quenching water is required. This represents an economy in power charges and in maintenance of necessary pumps, pipe lines, automatic valves, sprays, and similar equipment.

The best experience, available to date, indicates that after allowing for these reduced expenses, an additional charge of 1.5 cents per ton of coke should be made to cover necessary dry quenching maintenance.

### POWER

Electric power will be required for the coke elevating and handling equipment and also certain lighting charges must be made. A liberal figure is 0.4 kw.-hour per ton of coke cooled. Taking this at 1 cent per kw.-hour, the figure of \$4600 per year is obtained as given in Table III. For a plant of this size, it is estimated that about 1100 hp., would be required to operate the fans. Furnishing this power by means of a part of the steam produced from dry quenching, it seems, is the most economical method for a plant of this size. Taking 14 pounds of steam per horsepower-hour which is easily obtainable in a condensing turbine, it is found that about 370,000 pounds of steam per day will be necessary. This is equivalent to 110 pounds of steam per ton of coke cooled, which was the figure used above in arriving at the net steam produced. For such a turbine, condensing water, however, is necessary. This is taken at 800 gallons per minute, and a cost of 0.5 cent per M. gallons is used to cover the pumping of this water. Using these figures then, a total charge for condensing water of \$2000 per year is arrived at. The cost per M. pounds for the steam produced in excess of the plant requirements then becomes 2.93 cents.

### FIXED CHARGES

The cost of installation of a plant of this size has been rather carefully estimated and works out to be about \$525,000. If fixed charges be taken at 16 per cent annually, the yearly charge then due to this item becomes as given in Table III, \$83,900 or is equivalent to a charge per M. pounds of steam of 8.65 cents. The total cost of steam, therefore, including 16 per cent fixed charges, becomes 11.58 cents per M. pounds.

A brief summary of this paper is given below:

1. The history of coke making shows the definite trend toward

conservation of energy and material, and dry quenching is a logical development along these lines.

2. Actual operating records from dry quenching plants show that the gross annual revenue from the steam—valued at 25 cents per M. pounds—produced by dry quenching all the by-product coke made in the United States in 1926, would be \$11,000,000.

3. The heat balance of the Rochester, N. Y., Dry Quenching Plant is given, in which it is pointed out that careful measurements have shown an average steam production of 1005 pounds per ton of coke cooled.

4. The question of coke dust is briefly discussed and experience is given to show that no operating difficulties occur due either to gas stoppages caused by dust or by abrasion resulting from dust.

5. There is a discussion of the advantage of producing a clean coke, either dry or with a very low and uniform moisture content. Coke breeze of from 2 to 4 per cent moisture is readily obtainable.

6. It is pointed out that in many cases there is a great advantage in the reduced travel of quenching car and in the reduced hot car and plant steelwork maintenance due to the elimination of quenching water with its attendant corrosive vapors and possibilities of cold weather freezing troubles.

7. Evidence is given to show that with the usual American quenching methods there is no fundamental difference in coke structure due to wet or dry quenching provided that both cokes are given the same amount of handling.

8. It is shown that due to the absence of wet breeze clinging to larger coke, better screening and preparation of coke results from dry quenching.

9. Evidence is given showing that the necessary additional handling involved in dry quenching produces smaller coke, which is, however, more uniform in size and physically stronger, therefore more resistant to further handling.

10. It is mentioned that American experience has shown about 5 per cent better water gas fuel economy from dry quenched coke than is obtained in wet quenched product.

11. Likewise, results are given showing that producers using small coke operate at approximately 5 per cent better efficiency if dry quenched coke be used.

12. It is pointed out that in view of better economies in producers and water gas machines, low and uniform moisture, and stronger

coke, better blast furnace fuel economy would seem to be inevitable if dry quenched coke be used. Although no actual American experience is yet available, European results have, however, shown from 2 to 5 per cent better blast furnace economy.

13. Consideration is given to various other uses of coke, such as for domestic consumption, for boilers, for foundries, and for industrial furnaces. For these uses, it is mentioned that dry quenching has the important advantages of producing coke uniform in size, free from adhering breeze, always low and uniform in moisture, and more resistant to further handling than the wet quenched product.

14. An economic study of a dry quenching plant is given, in which it is shown, that in an installation to handle in one unit 3300 net tons of coke daily, steam may be produced for \$0.0293 per M. pounds, exclusive of fixed charges, that fixed charges at 16 per cent annually amount to \$0.0865 per M. pounds, giving therefore, a total cost of steam of \$0.1158 per M. pounds.

#### DISCUSSION

H. J. ROSE (The Koppers Company Laboratories, Mellon Institute, Pittsburgh, Pa.): It is very gratifying to learn, even so late in the week, that such a thing as a high temperature carbonization industry does exist. Those who have attended previous meetings this week might not have realized this fact. Probably most of you know however that about one ton out of every seven tons of bituminous coal mined in this country is coked by high temperature processes.

There is a coke plant near Pittsburgh which carbonizes approximately one per cent of all the bituminous coal mined in the entire world!

It is evident that Mr. Evans, and his associates, are doing some very important and interesting work. There are a number of points that caught my attention in his talk.

The first point is the fact that there are statistical methods to study blast furnace data. Those who have unsuccessfully tried to make something out of a voluminous mass of blast furnace data, will realize that statistical methods are necessary for this type of problem.

Unfortunately, chemists and engineers do not know as much about statistical methods as they should. Mr. Evans has told me that he employed a biologist for this work. I think that there may be a certain advantage in having the work done by a man without previously formed opinions.

The curve illustrating the effect of moisture on the efficiency of blast furnaces is very interesting indeed, and especially since there are now several commercial processes for gas and air dehydration. This is a subject which certainly deserves further study.

The time is so short that I will not say more about this paper. I expect to study Professor Terres' paper with a great deal of care. It is only through the

most careful study that it will be possible to realize the full value of this splendid paper. Although I have not had the privilege of reading it beforehand, I feel that it is going to prove a very real contribution to the scientific aspects of the industry.

Mr. Wilson has issued a challenge on heat conservation and his points are well taken. I have had the privilege of visiting the Rochester dry quenching plant several times. Mr. C. C. Russell, who is here today, assisted in making the tests on the strength of the coke, to which Mr. Wilson referred.

On the basis of these tests I would like to point out that the size of the dry quenched coke as produced due to rough handling, is very much smaller than the wet quenched coke, at least in the case of two different types of coke which were produced there. It would be very easy indeed, under such conditions, to get a debit, due to the small size of the coke, that would more than wipe out the credit due to the steam generated. Under certain conditions as at Rochester the smaller size of the coke may not be an important point. Under other conditions it would be a vital and determining factor.

DR. A. C. FIELDNER (Bureau of Mines, Washington, D. C.): I wish to compliment Mr. Evans on having shown a tangible relation between some of the physical properties of coke and its performance in the blast furnace. The application of the statistical investigative methods of the biologist was suggested, no doubt, because of the temperamental behavior of most furnaces. The many factors entering into blast furnace performance make it impossible to draw conclusions from a few observations. Perrott, Kinney and Joseph of the Bureau of Mines were unable to find any systematic relation between physical properties of coke and blast furnace performance in data collected from 13 different furnaces. It is possible that their failure to obtain correlation may have been due to the existence of a much smaller range of variation in the physical properties of American blast furnace cokes than is the case with British and Continental coke. American coke oven superintendents exercise great pains to produce a coke of uniform and standard quality. The general availability of high-grade coking coals in the eastern half of the United States makes it easy to produce coke of uniform quality.

I wish to ask Mr. Evans whether he has made any similar statistical comparison in which the rumbler test was used as well as the shatter test. I also wish to express my very deep appreciation of the paper which Dr. Terres presented. It is, without doubt, the best fundamental contribution thus far made on the heat carbonization of coal.

MR. EVANS: With reference to the American and British cokes, I am most interested in what Dr. Fieldner said about that. British blast furnace managers have a task of very considerable difficulty. In one blast furnace alone a blast furnace manager might get 20 or 30 different cokes a week. In small plants in our country the cokes might vary from 45 to 50 and up to 80 shatter index. Therefore, the coke problem at home was really the most important to be tackled.

With reference to the rumbler and shatter test, the rumbler tests have been adopted officially by the German Iron Masters Association. If they take up a test that fact is good enough indication as to its practical value.

We are testing outside, and side by side with the shatter tests the rumbler test. We are finding if we take a definite size of screen as an index the two tests give somewhat parallel results.

D. C. PORTER (Consulting Engineer, Philadelphia, Pa.): I am particularly impressed by the paper of Dr. Terres. In fact, I have no hesitation in saying I consider it one of the greatest contributions to the fundamentals of the science of coal carbonization that we have had in a great many years.

I have had some occasion to study carefully myself the matter of the heat balance and the mechanism of carbonization and I have noticed particularly the lack of exact data on the heat expenditure in the process. I think we are to be congratulated on some fundamentally exact data on that subject.

I would like to ask Dr. Terres as to the influence of composition of the coal on the heat of coking, particularly the oxygen content, the natural or inherent oxygen content of the coal, also as to the influence of rate of coking, whether in the experimental apparatus, the rate of carbonization was maintained always the same.

DR. TERRES: While we are still investigating the problem, I can say now that there is no direct relation between the heat of coking and the composition of a coal. Most of our tests have been made with lignites, on brown coal, and wood, the younger coals, as we call them. Generally, I do not believe our brown coal and our lignites are younger than our "Steinkohlen" (bituminous coals) as we call them. I do not believe a brown coal will become bituminous coal in a million years.

There are no direct connections between the coking heats and the composition of a coal, but the younger coals give higher decomposition heats, higher values for the decomposition heats.

Also, in the actual value of the coking heat there is not a very large difference. The differences in the coking heat are caused only, I think, by the character of the bituminous matter.

What do you mean by rate of carbonization? Do you refer to a state of coking?

MR. PORTER: The speed or the rate at which the heat is put into the coal as it is carbonizing.

DR. TERRES: There is no relation between the composition of the coal, coking rate and the conductivity.

MR. PORTER: I wanted to know whether your 15 grams sample of coal was coked, say in ten minutes or in two minutes.

DR. TERRES: That will not change the values of the coking heat, not at all. The speed of the carbonization is in no way related to the value of the coking heat. We measure only the quantities of heat. The coking rate is of some importance for the calibration of our apparatus. At first our calibration was arranged in such a manner that we were dependent on the quantity of the heat

sent into the apparatus in a unit of time, but now with the new apparatus and the new method of calibration we are independent of that. We are only dependent upon the total quantity of heat sent in.

In conclusion I wanted to add a few words about my curve of conductivity. I have shown you a regular curve of conductivity of the values between zero degrees and 1,000 degrees. It may be there is an irregularity in the curves, in the melting point of the coal let us say, the points where the coal goes into the plastic stage.

It seems to be so but we are not quite sure. But even if this be so, it will not change considerably the mean value from zero to 1,000 degrees. That is to say, in the calculation it will not change very much. It is possible that there may be an irregularity. We are now in the process of going after these measurements. They are very difficult because we must transform coal into coke under the same conditions and it takes a long time to transform a coal into coke under definite conditions using a temperature of about 300 or 400 degrees.

DR. T. SCHUMANN (Combustion Utilities Corporation, Linden, N. J.): My question concerns that very point. We carried on experiments of measuring the conductivity of coke and coal. I was surprised to find that the conductivity goes up smoothly according to Professor Terres' curve. According to our results we found that coal in the granular state, or in the state of lumps, has a conductivity of about one-third to one-fourth as great as that of monolithic coke, that is, coke in one lump.

I should have expected that curve to go up to the melting point and take a sharp rise there. My question was concerning that.

DR. TERRES: We are doing that. I have only shown a small part of our investigations because the time is too short to show all of it. You have seen our measurements with different grades of fineness of coke, and measurements with different grades of fineness of coal. The relation of the sizes of the grains is opposite there. We can explain that.

When we have larger sizes of grains, we should have lower conductivity because of the size of the grains. But in reality we measure a higher conductivity. The heat remains at the surface and therefore the transmission measured is at first too large. It does not go into the interior of the grains.

We also have measurements on this point. We can avoid this influence by employing more thermocouples. When the thickness of the material to be investigated is greater this influence will set it at a definite distance from the heating surface. We have measurements on this point.

CHAIRMAN BURKE: I realize fully the difficulties that Professor Terres is suggesting here. We have carried out a considerable amount of work in our laboratories on these same questions. The difficulties are tremendous.

J. E. DAVIS: Some years ago we determined the primary heat of decomposition of some representative American coals using a direct calorimetric method. We found the problem far from simple and I can well appreciate, therefore the experimental difficulties Dr. Terres must have encountered in extending his values over the whole carbonization range, determining not only

the decomposition heat but the coking heat as well. In fact he has gone further and determined the rate of heat flow into the coking charge and from this and the coking heat, calculated the coking time. I wish to compliment him on the thorough manner in which he is handling the problem.

The amount of heat which German practice indicates as required to coke coal, converted into English units is as follows: 12 kilos of coke per 100 kilos of coal for underfiring means about 250 pounds of coke per ton of 2,000 pounds and 11.5 kilos means about 230 pounds per ton. The 955 calories per kilo of coal carbonized is equivalent to 1,719 B.t.u. per pound or 3,800 cubic feet of 540 B.t.u. gas per ton of coal carbonized. The 50 cubic meters of mixed gas per 100 kilos is equivalent to 16,000 cubic feet per ton; 1,133 calories is 2,040 B.t.u. per pound and 850 calories corresponds to 1,530 B.t.u. It may be pointed out that the recent American Gas Association carbonization tests show, according to Ward, that the coke required for underfiring varied from 230 to 318 pounds per ton of coal. These figures, perhaps, represent the average rather than the best American practice, since some of the equipment used was old and hence not so efficient as new apparatus.

The coking heats found by Dr. Terres vary quite widely with the kind of coal, as I think one would expect. The result involves not only the decomposition heats, which are variable, but also the sensible and latent heats which do not necessarily vary in the same direction as the decomposition heats. The factors involved in the summation are very complex. I do not know that I understand clearly what Dr. Terres' coking heat includes, but take it from his definition that all the latent and sensible heats of the products from 20°C. to the temperature in question are figured as heat expended. If one were to use the dry quenching process, therefore, such as described in the paper by Mr. Wilson, quite a large portion, nearly 40 per cent, of this heat would be recovered in usable form.

The decomposition heats for the primary decomposition range of German coals appear to be of the same order of magnitude as those found by us for American coals. I am somewhat surprised to find, however, that positive decomposition heats are found at temperatures as high as 1,000°C. Such evidence as we obtained indicated absorption of heat by secondary decomposition; e.g., endothermic decomposition of tars, gases and pitches. However it must be admitted that our data did not extend to very high temperatures and furthermore, German coals may behave differently from ours.

I want to emphasize one point here that seems to have been brought out pretty clearly in our experience. The summation of reaction heats up to a certain maximum carbonization temperature is not necessarily constant for a given coal. Other factors beside the temperature are involved and the manner in which the temperature range is covered makes a difference in the final result. For example, with a rapid heating rate one gets somewhat different reaction products than at slower rates; the summation of reaction heats must therefore differ in the two cases. We tried carbonization in stages in our calorimeter, cooling down between stages before heating to the next higher temperature. The resulting sum of reaction heats was considerably lower than that obtained by heating over the whole temperature range in one step. This could have been caused by the slow heating rate or by secondary decomposition of tar

vapors condensed in the heating zone by the successive coolings. I do not know to what extent the heating rate factor was operative, but it has been our invariable experience that secondary decomposition is attended by heat absorption.

I wish also to refer to another finding of ours and this is that the alpha and beta compounds separated from coal by pyridine extraction are exothermic over the primary carbonization range, whereas the gamma compounds are endothermic. The latter are, according to Illingsworth and others, responsible for coke cementation. The coke cementation process is therefore probably endothermic.

American engineers will probably be most interested in Dr. Terres' coking heat figures at around 1,000°C. It may be worth while, therefore to convert them into English units. They are as follows:

COAL	CAL./KGM.	B.T.U./LB.	LIBS. 14,000 B.T.U. COKE
Saar.....	217	391	56
Stinnes, Ruhr.....	370	628	90
Prussian coking.....	308	554	79
Dahlbusch.....	420	756	108
English, Easington 1,000°.....	330	562	80
English, Easington, 1,050.....	560	1,000	143

CHAIRMAN BURKE: I think that probably the explanation you note, Dr. Davis, is quite as you suggest. I am referring to the fact that you did not find exothermic reactions at the high temperature ranges. As I recall it your work was done holding the tar in the calorimeter during the entire heating. Professor Terres' work was done by permitting the tar to come out of the calorimeter.

We carried out a similar study which has been published. It is on the heat of distillation, as we call it, or the heat of coking using a method similar to that of Professor Terres. Subsequently, we had occasion to study the conductivity, or rather the diffusivity of cokes formed and different temperatures. We did that by taking the monolithic coke structure that had been formed by carbonization and plunging it into the furnaces, the wall temperatures of which were maintained at a definite temperature.

We had coked the coal up to a temperature of 700°C. The monolithic coke was then plunged into another furnace at 800°C., the wall being maintained constantly at a temperature of 800°. Then we followed the temperature at the center of the coke and found to our astonishment that it went higher than 800°. That shows clearly that there were exothermic actions.

We followed that up with different temperatures and the results of those studies will be published. I think the suggestion you make is the correct one. It is due to thermal decomposition of the tar in the calorimeter that those reactions are endothermic which makes following it up impossible.

DR. TERRES: Regarding the magnitude of the value of the coking heat, was that at a higher magnitude?

CHAIRMAN BURKE: I have not them in mind. I had not seen your paper until the last evening and I did not come prepared with our values. As near as I can recollect, they agree very closely with those which you have obtained. I will say however, that none of our calculations of the heat of decomposition appear to be quite as large as those that you have obtained.

I think Dr. Davis will bear me out on that as far as the general run of American coals are concerned. Does it not appear to you that the results that Professor Terres has obtained are somewhat larger, both positive and negative, than those that we have obtained with American coals?

J. E. DAVIS: I think Mr. Wilson's paper is very informative on a process new to this country which has two attractive features: (1) the very obvious one of improved heat utilization, and (2) improvement of the product. This last may be somewhat debatable depending on the use to which the coke is to be put. However the speaker has convinced me that he can produce a coke exceptionally uniform in quality particularly as regards moisture content of all sizes and I can not think of a use for coke where I would not greatly prefer it uniform if I could have it so. He further shows that recovery of the heat as steam costs considerably less than the heat is worth in this form. I have only a few specific comments to make.

I take it from the heat balance that the heat recovered as steam is 1,217,000 less 190,000 + 153,000, which is 67 per cent of the sensible heat of the coke. This seems to me good performance for apparatus of this kind.

Even if some coke is consumed in the extractor (in addition to the volatile matter) it does not seem to me that this can be of greater importance than that burned by exposure of hot coke before quenching in the usual process. Devolatilization in the extractor might well result in improved coke quality, I think.

Treatment of the hot coke in the extractor, even for the short time required to transfer its sensible heat might be expected to activate it rendering it more combustible. I would like to ask Mr. Wilson if he has noticed that this coke is better than wet quenched coke in this respect. According to the argument of low temperature advocates a reactive or combustible coke is highly desirable.

For blast furnace use I do not think the point made as to importance of uniformity of fuel can be too strongly stressed. Uniformity makes for certainty of control which enables maximum furnace capacity to be realized day in and day out. This is important and hard to attain with a large unit such as a blast furnace when raw materials are varying.

MR. WILSON: I am sorry that I have no information available on that. As far as I know no comparative tests have been made and no operating experience is available that is of a sort to make comparison possible, that is, a comparison that would be of any value.

# PROGRESS MADE IN THE MANUFACTURE OF FOUNDRY COKE BY A NEW SYSTEM OF COAL CARBONIZATION

By JULIEN PIETERS

*Paris*

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Every one connected with the coal trade knows the inherent characteristics and faults of the two systems of low and high temperature carbonization. Engineers all over the world have been searching for ways and means of improving both these processes yet the construction of the oven itself opposed any radical improvements.

Low temperature carbonization installations are very costly, and require constant renewal. They produce a much higher yield of tar products but the gas production is considerably decreased and very little ammonia liquor can be recovered. Further the coke is of very little commercial value, valueless as a foundry coke, and owing to a large quantity of breeze it is a very inferior fuel for domestic purposes.

The last twenty-year period has seen few changes in the construction of high temperature installations. Certain modifications in details had increased the production per retort, but the coke-oven remained a most expensive means of treating coal and an ideal apparatus to destroy the tar by-products. The phenomenon of coal distillation, which in itself does not absorb any energy but on the contrary produces an enormous quantity of heat, demands, in even the most up-to-date coke-oven, heat which is generally not less than 2,200,000 to 2,400,000 B.t.u. per ton of coal treated.

Owing to the very high temperature at which the gas leaves the oven, the output of by-products is relatively low, while their decomposition, particularly of the tar oils, is very great.

The present oven is realized to be an uneconomical apparatus and it is difficult to remove these inherent defects without modifying it completely, not only as to its construction, but also as to its system and its method of working.

After many years of working, a new type of oven has been devised, altogether new in construction, and based on entirely new principles.

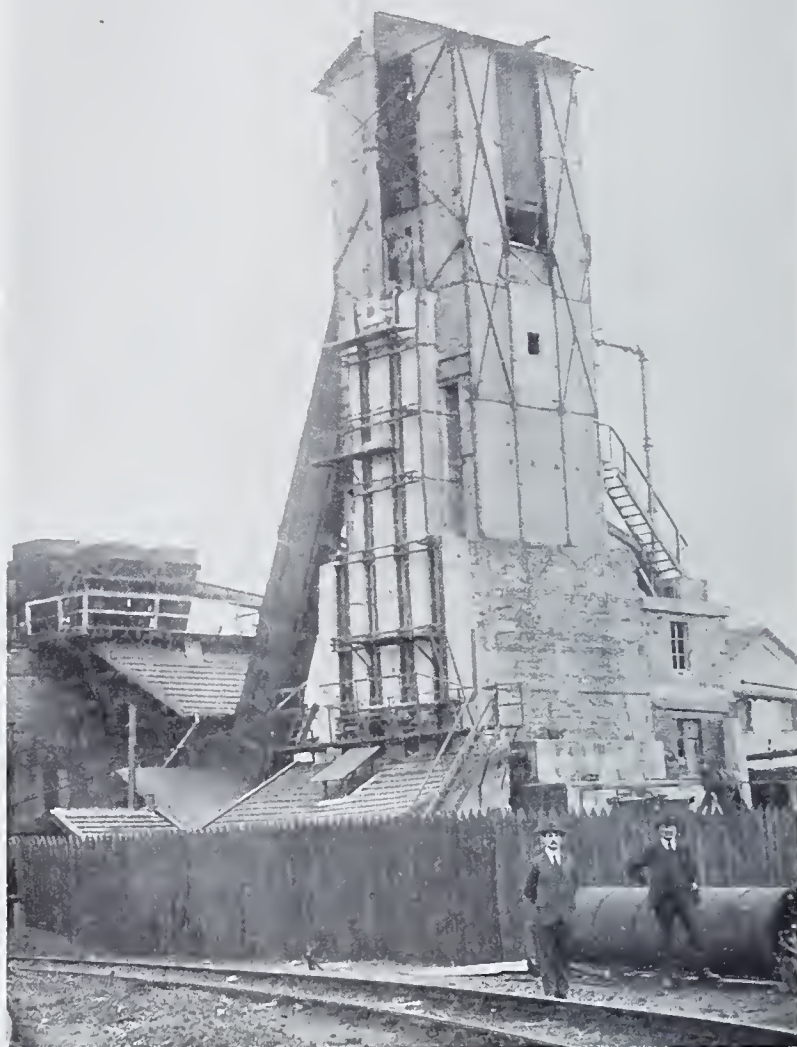


FIG. 1. FIRST EXPERIMENTAL-OVEN (10 TONS PER DAY) ERECTED AT LE BOUCAU (FRANCE) IN OPERATION FROM THE BEGINNING OF 1919 TO END OF 1925

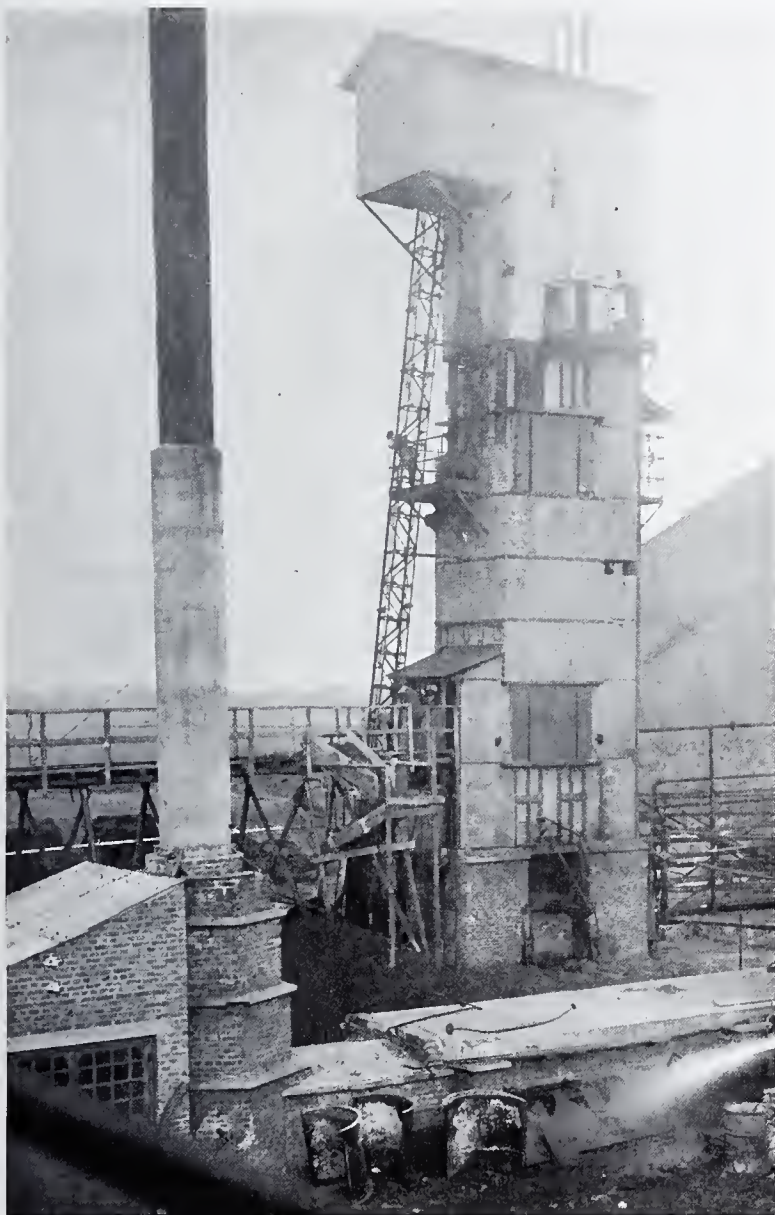


FIG. 2. DEMONSTRATION-OVEN (10 TONS PER DAY) ERECTED AT MONTÉGNÉE  
(NEAR LIÈGE, BELGIUM) IN OPERATION SINCE END OF 1926

While low temperature carbonization is maintained at about 1022° F. and high temperature carbonization at about 1742°F. the Pieters new carbonization process is a progressive and continuous one, start-

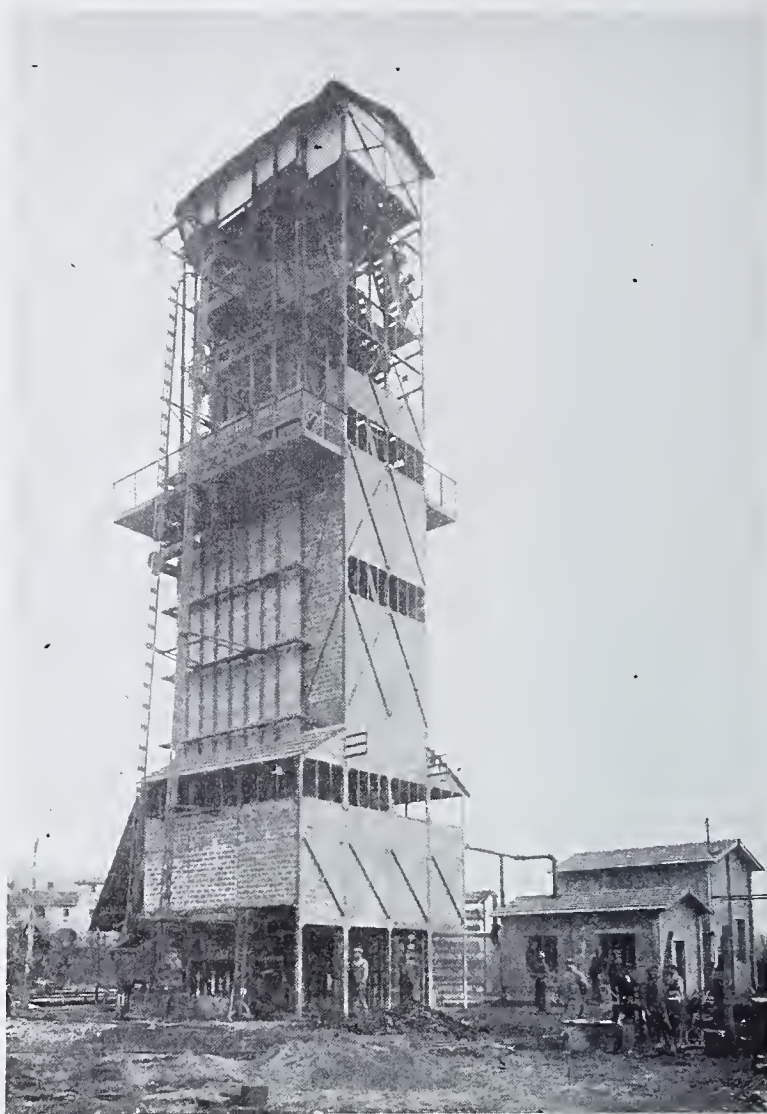


FIG. 3. INDUSTRIAL-OVEN (50 TONS PER DAY) ERECTED AT SAN GIOVANNI VALDARNO (ITALY); WORKING SINCE BEGINNING OF 1928

ing at about 212°F. and finishing at 1472° to 1742°F. according to the particular quality of coke required. The coal, therefore, passes through the zone of low temperature carbonization, through the in-

termediary zones of carbonization, ultimately reaching the zone of high temperature carbonization, with the result that the process of coal distillation is improved in a very important manner.

Numerous laboratory trials showed the many advantages of this new system of distillation, and proved that such a process could only be conducted in a vertical continuous oven. In 1919 at Le Boucau (France) a trial oven of a capacity of ten tons in 24 hours was built (Fig. 1). In 1925 a new demonstration oven of the same capacity as the one at Boucau, but incorporating the improvements suggested by the working of it, was built at Liège (Belgium), in order that there could be attempted a new process of treating all kinds of coals and other combustibles, which had been previously considered unsuitable for the manufacture of metallurgical coke (Fig. 2). The results have been most satisfactory, because even from this so-called non-coking coal a product quite equal to, and to all intents and purposes, even of a better quality than metallurgical coke has been manufactured.

These results have been obtained industrially with all the different classes of combustibles, such as bituminous, gas, coking and dry coals, anthracites, lignites, peat, wood and even sawdust and this is easily explained if all the agents which exercise an influence on the phenomenon of coke formation or agglutination of combustibles are taken into consideration, namely:

### 1. THEIR PHYSICAL STATE

The coal, when mined is not absolutely homogeneous, even when it consists of very small pieces. When closely examined one will notice very small layers of inert matter intermixed with the coal particles. Even taking coal from the same seam or pit, important differences will be noticed between one piece of coal and another. These differences are still greater when taking pieces from different seams, even if they are very close to each other. It is therefore clear that where the coal has a different structure its agglutinating power will be different as well.

To obtain a regular quality of coke, it will therefore be necessary to arrive at a homogeneity of the coal mass. This is obtained by reducing the coal to a very fine powder.

The influence of the homogeneous character is already well known to all the coke manufacturers, and in all coke works the coal is crushed before it is introduced into the oven.

## 2. THE PRESSURE TO WHICH THE COAL IS SUBMITTED DURING DISTILLATION

It will be understood that any pressure exercised on the coal during distillation causes its minute particles to be brought together and facilitates the reunion of these particles with the assistance of the coking materials.

This phenomenon is utilized to a certain extent in the ordinary cokeworks, where the high volatile coals are pressed into the oven. To arrive, however, at a better result, it will be necessary to maintain this pressure even in the oven itself during the distillation, as the liberation of the gas has the effect of quickly destroying the cohesion obtained by the pounding, scattering afresh the minute particles of the coal.

## 3. THE PROCESS OF DISTILLATION

Numerous experiments made by the Société "Le Coke Métallurgique" of France, when investigating the best process of coking the coals from the Sarre district, have shown that a slow and progressive distillation, applied especially to high volatile coals, resulted in improving the quality of the coke and particularly increased the hardness of it.

This can easily be explained, if one considers that in such a process of distillation the liberation of the gas is much slower and more regular, while by a rapid distillation the tumultuous liberation of the gas produces the separation of the coal particles and causes an increase of fissures in the coke, making it very brittle in consequence.

In a general way slow and progressive distillation increases the quality of the coke, whatever the nature of the coal may be, while the opinion often expressed that the coal must be "vigorously and briskly coked" does not at all agree with the facts. Even to-day no coke-oven, even completely charged with coal, allows this to happen, because although the outside of the body near the walls is rapidly coked, the interior must of necessity be coked slowly. It is an observed fact that the exterior portion of the coke-body, which has been coked vigorously and quickly, is very much more fissured than the remaining portion of the coke-body.

## 4. THE AGGLUTINATING POWER

Certain coals have too high an agglutinating power, that is to say that they give a coke entirely molten and strongly fissured. This

can be ameliorated by adding to it some dry coal. One arrives in this way to the converse statement that "one can coke dry coals by adding to them the agglutination which they lack."

Now this agglutination comes from the decomposition of the heavy hydrocarbons and is created by the carbon in its nascent stage, which possesses the property of uniting the carbon particles together.

My personal experience has been that any heavy oil increases this agglutinating power. This increase is at its maximum with the heaviest hydrocarbons, viz., with pitch, which liberates the maximum proportion of free carbon when heated to a high temperature, where it undergoes the phenomenon of cracking while the heavy oils volatilize and partly escape in the cracking process.

The pitch itself presents a superior agglutinating power when it has been previously oxidized. In this case its decomposition is facilitated by the presence of hydroxyl groups, which causes the formation of water, carrying off the combined hydrogen from the carbon, which is liberated in this way.

Other experimentalists such as Messrs. Hennebutte and Goutal of France have ascertained the same results in their manufacture of "Carbonite," which is a real coke obtained from charcoal powder, to which has been added oxidized pitch, obtained by preference from wood tar.

All the above indicated facts are assembled in my process and the oven permits in this way the transformation of any combustible, including real coking coals, under economical conditions.

#### CHARACTERISTICS OF THIS NEW OVEN AND PROCESS

There already are several different systems of continuous vertical ovens, some of which have made good headway, more particularly for the manufacture of illuminating gas.

The oven under consideration possesses however altogether new features of very great importance, both as to its calorific economy and increased output, while its cost of construction and maintenance is much lower.

The oven differs from other coke or gas ovens by the following characteristics:

a. Its system of continuous recuperation of the total heat in the coke by exterior conductibility and by direct interior contact with the cooling coke mass. This process of recuperation constitutes a very powerful and very economical way of firing.

On account of the continuity of the oven and its rapidly decreasing temperature from bottom to top, the quantity of heat contained in the fumes is very much lower than those of the ordinary coke or gas ovens.

b. Its system of progressive operation.

c. Its special and altogether new flue construction, in order to obtain a very quick firing as well as a rapid decrease of the temperature from bottom to top. This construction assures a great tightness and is realized by small specially shaped bricks, that are much cheaper than the large ones used in other retorts.

d. Its discharging system. The coke is discharged with the aid of two separate registers, one of which supports the coke body and the other of which secures an absolutely tight joint at the outlet of the oven.

e. Its special treatment of all combustibles, producing from them, after recovery of all the by-products, a new fuel having all the characteristics of metallurgical coke or anthracite, even from those which are of a non-coking nature.

These coals, mixed with a small percentage of pitch, are first agglomerated into briquettes of the size required for the purpose by the ordinary process. The agglomerates are then put into the oven and treated. The pitch is completely cracked during distillation; about 50 per cent is recovered in the form of oils, about 40 per cent as non-condensable gas, while only about 10 per cent remains in the briquette in the form of carbon, which cements the coal particles producing a very hard patent fuel.

This process avoids the production of any waste or breeze and the foundry coke is superior to that obtained in the ordinary coke-oven.

Notwithstanding the seeming complication of this treatment it is very economical on account of the complete recovery of all the products and the total absence of any loss of heat during distillation, while a first class metallurgical coke is manufactured from any and every quality of coal. The fuel so obtained is very hard and can be used for all metallurgical, industrial and domestic purposes. As a smokeless fuel for bunkers, on railways and in gas-producers it finds use according to the quality produced and required.

#### SUPERIORITY OF COKE PRODUCED IN A DETERMINED SIZE

The coke obtained by this process is in lumps of a fixed size, which will assure a far superior economical result in the blast-furnace.

The coke, manufactured by the ordinary processes and ovens at present, is composed of lumps of all dimensions, from 1 to 12 inches in size, while during the necessary manipulations of it the proportion of small coke and breeze becomes greater and greater. At the moment it is introduced into the blast-furnace, this coke of very irregular composition distributed itself in a very irregular manner. The large lumps, as everybody knows, run towards the edge of the heap, while the small coke and breeze settle themselves nearly vertically down the charging hole.

Each succeeding load behaves similarly, without it being possible to arrange for any proper mixing, with the result that the charge of the blast-furnace presents vertical zones or belts composed of lumps decreasing in size from the outside to the center. The consequence is that gas more easily penetrates the zones of the large lumps than the zones of the smaller coke and breeze, so that a much larger quantity of air passes through the former and produces a much more violent combustion. Similarly the carbon monoxide formed traverses more easily the exterior zones than the other ones. A large quantity of carbon monoxide, which constitutes the principal reducing agent, escapes, therefore, without functioning in the blast-furnace, causing an important loss in carbon, that is to say, coke, which has, in consequence, to be charged in larger quantities, so as to compensate for this loss in carbon monoxide. Theoretically only half the quantity of coke charged is required to produce the required reactions as well as the fusion of the masses; in other words the calorific energy contained in the gas which escapes from the blast-furnaces represents more than half the quantity of the total energy supplied.

I estimate that in practice it will be possible to recuperate half of this lost energy, reducing in this way the consumption of the blast-furnace by about 25 per cent of the weight of the coke actually shipped. This can be realized by charging only lumps of coke and ore all of the same size, so as to obtain a homogeneous mass in the furnace. It will of course be necessary to insure that the coke is sufficiently hard and shock resisting so that its dimensions are not reduced during the different manipulations prior to its entry into the furnace. Coke manufactured according to this new process possesses this quality.

The reactivity of coke depends to a large extent on the area of the exterior surface. Given small hard round lumps which can be charged into the blast-furnace without breaking, the aggregate surface will

be considerably greater than an equivalent weight of ordinary heterogeneous coke, with the result that its reactivity will be proportionately greater.

#### DESCRIPTION OF THE OVEN AND ITS PROCESSES (SEE FIG. 4)

The combustible coming from the storage hopper is brought to the top of the oven by bucket elevators or automatic skips and drops directly into sheet iron hoppers (*A*) which constitute an elongation of the actual retorts. These take the form of vertical cavities (*B*) of which the width is slightly less than the width of the ordinary coke-oven. They are open at the upper part but hermetically sealed at the lower.

While the plant is in operation these vertical retorts are closed in the upper part by the coal body, rendering them completely gas tight. A damper (*D*) however, can be used to isolate each of the elements, if desired.

The downward movement of the coal-body through the retort is regulated by the rate at which the coke is drawn off from the bottom.

The coal commences to be heated gradually as it passes downwards through the retort, and the zone of low temperature is sufficiently large to allow the separation of the oils and other by-products and to avoid all over-heating.

The temperature of the retort is gradually increased and the coal on its downward path passes through different zones, where the temperature is gradually raised. In this way a systematic exchange of heat between the flues of the oven and the combustible under carbonization is created, which is eminently favorable to a large coke-output as well as to a high yield of by-products.

To obtain the above results, the generating gas is made to follow a zigzag path brought about by the special construction of the flue. The continual change in the direction of the flow results in the acceleration of combustion and increases considerably the heat transmission between the flames and the brick.

When the coke arrives at the zone of the highest temperature (*F*) it is completely finished. Continuing its downward movement it undergoes then a cooling process by the circulation of a gas current through the flue chambers constructed in the lower part of the oven as well as by a gas-stream circulating through the whole coke-body from the bottom to the top.

The coke thus arrives at the discharging apparatus (*G*) at a tem-

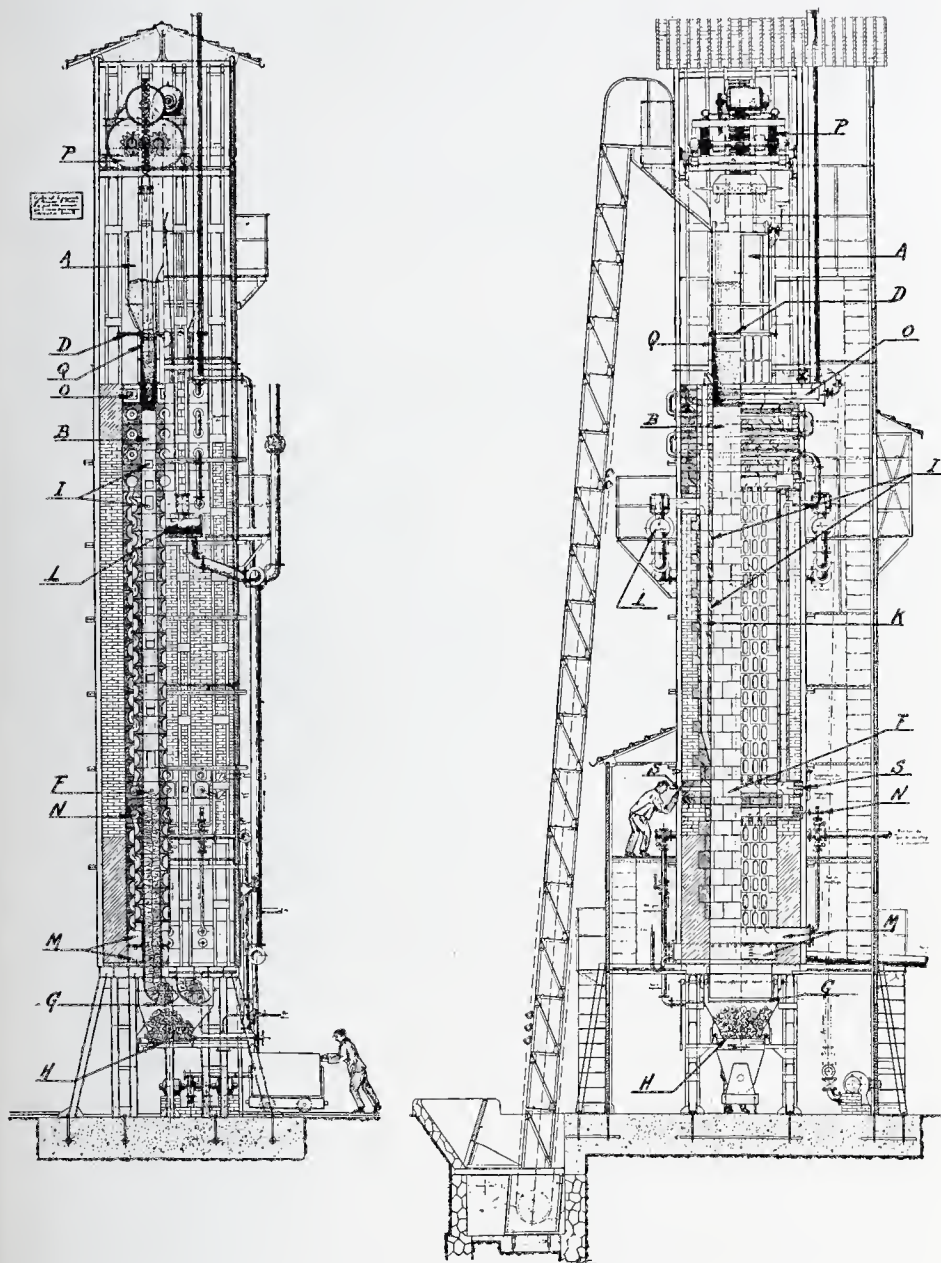


FIG. 4. PIETERS' CONTINUOUS FURNACE FOR THE DISTILLATION OF COALS  
AND THE MANUFACTURE OF METALLURGICAL COKE

perature very little higher than that of the atmosphere. The discharging of the coke at regular intervals takes place through two registers, one of which supports the coke-body and the other secures an absolutely tight joint at the bottom of the oven.

The first register (*G*) is an oscillating sheet iron basket, the curve of which is identical with the lower part of the retort, under which it is arranged to swing, thus discharging its coke-content. The second register (*H*) is a movable flat slide valve provided with a hydraulic seal.

The gas leaves the retort by a certain number of apertures (*I*) arranged along the walls of each retort. Vertical columns (*K*) carry them into a main (*L*) connected with the general pipe range leading towards the by-product works.

The gas, required for heating purposes, picks up the heat from the finished coke and is divided into two separate lines of flow, entering into two separate cast iron chambers (*M*) at the base of the oven, just above the discharging apparatus. One of these flows passes through the coke-mass, and the other through the recuperating flues, which constitute the lower part of the retort. The former recuperates the heat by direct contact with the coke, is unlimited in quantity and therefore thoroughly cools down the coke while the latter recuperates the heat by transmission through the brickwork, and is limited in quantity, being used only for heating purposes.

After its passage the gas is mingled with the air in the combustion chamber (*N*) at the zone of the highest temperature (*F*).

The air required for the combustion enters the retort at the upper end of the oven (*O*) where it carries away the major portion of the sensible heat of the fumes and is made to traverse a path in opposition to that of the ascending waste heat and to descend through a special chamber which runs parallel to the firing flues, finally entering in a preheated state with the gas into the combustion chamber (*N*).

The oven can also be heated with gas from a gas producer or blast-furnace.

Suitable openings (*S*) are arranged for observation of the temperature in the main combustion chamber, and pyrometers are fixed so that the control of the temperature can be efficiently regulated.

When directly treating a coking-coal the regular progressive movement of the coal body is obtained through the medium of a hollow piston (*Q*) operated by gearing (*P*) carried on a framework in the

upper part of the oven structure and which can be moved on rails so as to operate over any of the retorts. The lower edge of the piston is knife shaped, forming a cutting edge, which, during the downward movement, shears a clearance space between the descending coal body and the sides of the retort chamber.

The hollow piston is designed in such a way that its downward movement gives sufficient pressure to carry forward the coal body but does not allow this pressure to reflect dangerously on the discharging machinery at the base of the oven.

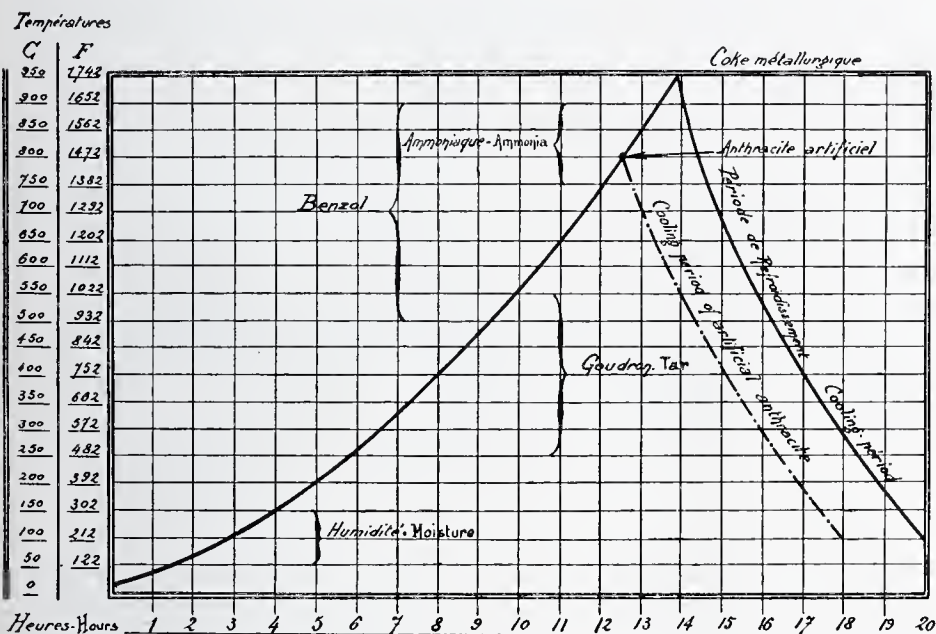


FIG. 5. PIETERS' CONTINUOUS FURNACE PROCESS OF DISTILLATION

The operation of the piston coincides with the discharge of the coke at the base of the retort.

If one is required to manufacture a coke strictly of the same size, which presents very great advantages from a metallurgical point of view, this apparatus for a progressive movement becomes unnecessary and the oven is accordingly much simplified, as the fuel treated descends easily and in a very regular manner.

The brickwork of the oven can be repaired with ease at any point. A series of drastic tests designed to cause distortion or cracking of the brickworks have so far failed to cause any damage to the bricks.

The flue-joints during these tests remained perfectly tight, although means to cause distortion and leakage were resorted to. Figure 5 shows the process of distillation and cooling of the combustible. The charge is put into the retort at a very low temperature ( $122^{\circ}\text{F.}$ ). The first action of the heat is to drive off the moisture and hygroscopic water. As the coal runs down into a temperature of  $572^{\circ}$  to  $662^{\circ}\text{F.}$  it becomes semi-fluid and decomposition of all the coal bodies commences rapidly, increasing in vigor with each accession of heat; the fluid tar, the slightly viscid tar from the resinoid bodies and the rich heavy tar from the hydrocarbon gases go forward immediately as vapors with the gases through the apertures arranged for at small intervals in the retort and connected with the gas-main, while the pitch, which is left, binds the half-coked coal. As the coal arrives at the hotter zones of more than  $1292^{\circ}\text{F.}$  the residues in the semi-coke and pitch further decompose until only the hard coke is left, which consists of little else than carbon, ash and traces of hydrogen, either combined still or occluded by the coal.

As the coal passes through the  $932^{\circ}\text{F.}$  zone the benzol begins to appear in the gas while at the  $1382^{\circ}\text{F.}$  zone the ammonia vapors commence to disengage themselves and both are completely recovered when the coke process has finished.

#### PRACTICAL RESULTS OBTAINED

The following results have been obtained:

A Newcastle coking coal gave a coke of a superior hardness and density. The crushing resistance of three trials gave an average of 270 kgm. per  $\text{cm}^2$  (3713 pounds per square inch) while the coke produced from the same coal treated in the ordinary coke-oven only had a crushing resistance of 140 kgm. per  $\text{cm}^2$  (1948 pounds per square inch).

The gas consumption of the oven has been determined and is an important economic factor. Forty tons of coal of 20 per cent volatile and 10 per cent moisture treated in 24 hours, required for firing purposes less than 200,000 calories per ton of coal treated or 1773 cubic feet of gas at 4000 cal./ $\text{M}^3$ . (The ordinary coke oven uses about three times as much.) This result will be still further improved when using a larger capacity oven.

This low gas consumption is fully explained by analyzing all the losses of heat; viz.:

The coke left the oven at a temperature of less than 122°F. on an average. The temperature of the fumes did not exceed 302°F. The loss of heat by exterior radiation was estimated not to exceed 80,000 B.t.u. per ton and moreover the direct losses of gas at the moment of charging the oven as well as gas escape through the doors of the ordinary coke-oven are completely abolished.

TABLE I

COMPARATIVE RESULTS OF THE CARBONIZATION OF A BITUMINOUS COAL OF 35 PER CENT VOLATILE MATTER

	LOW TEM- PERATURE CARBONI- ZATION, 1022°F., PER 2240 POUNDS	HIGH TEMPERATURE CARBONIZATION, 1742°F., PER 2240 POUNDS	CARBONIZATION PROCESS, J. PIETERS, PER 2240 POUNDS
Benzol and Motor spirit, gal- lons.....	5.64	2.82	5.64
Middle and heavy oils, gal- lons.....	13.53	4.51	13.53
Naphthalene and anthra- cene, pounds.....	4.51	9.02	None
Total tar products, gallons..	20.30	12.63	19.85
Pitch, pounds.....	18.00	49.61	18.00
Gas production, cubic feet...	3,594	11,500*	10,782*
Gas available after firing of the ovens, cubic feet.....	None	5,750	8,086
Sulphate of ammonia, pounds.....	None	22.55	27.06
Coke, hundredweight.....	14.50	13.30	13.30
Quality of the coke.....	Pow- dery	Very much swol- len, very little resistant, much breeze	Dense, very hard, regular good- sized pieces, no breeze

\* Cubic feet of 546 B.t.u.

The tar oils produced are much more fluid than those of the ordinary oven and are quite free from naphthalene. Their distillation in the laboratory up to a temperature of 662°F. showed not more than 10 per cent of pitch, while the tar obtained from the same coal in the ordinary coke-oven contained on an average 45 to 50 per cent of pitch and about 10 per cent of naphthalene.

Table I shows a typical example of the distillation of a bituminous coal of 35 per cent volatile matters carbonized by the low and the

high temperature processes as well as by this new process, proving that the latter secured the same quantity of oils and pitch as obtained by the low temperature carbonization and that the gas, coke and sulphate of ammonia obtained by the high temperature carbonization were also obtained by this new process. Moreover the coke obtained by this latter process was dense and very hard without any waste or breeze, whereas the coke obtained by the high temperature carbonization was greatly swollen with very little resistance and contained a large quantity of waste and breeze.

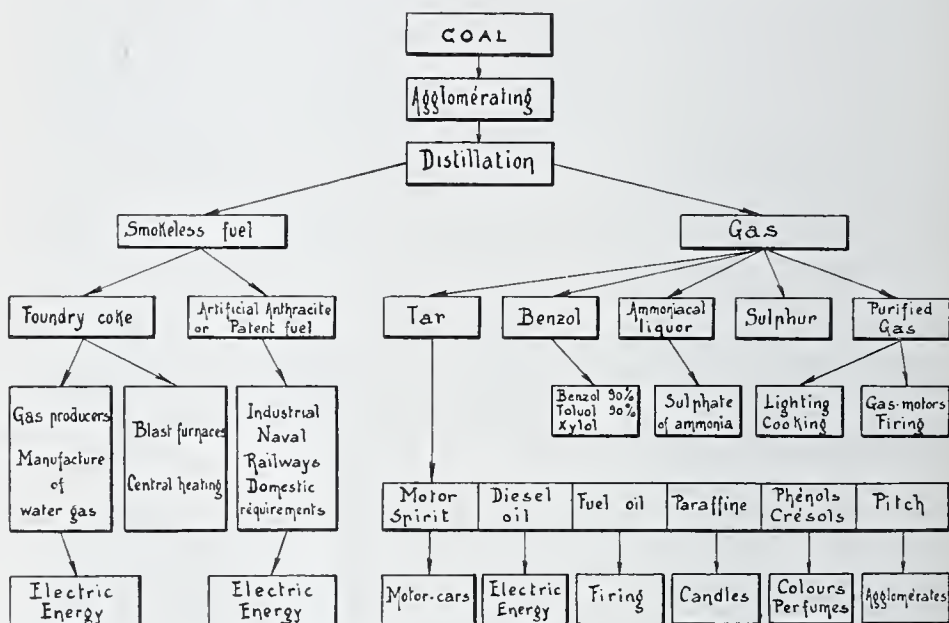


FIG. 6. TABLE OF PRODUCTS OBTAINED BY THE DISTILLATION OF BITUMINOUS COALS

Further the great economy in heating of this new process is proved by the quantity of gas available after firing the oven, which was 8086 cubic feet against only 5750 cubic feet by a high temperature carbonization.

Summarizing the advantages of this process, they are:

1. Ground space one-fifth to one-sixth of what is required for an ordinary coke oven plant.

2. Foundation cost 60 per cent less.

3. Quality of gas very regular.

4. Great economy in gas consumption.

5. Better quality of coke and very regular.
6. No quenching water required.
7. Benzol and sulphate of ammonia output increased.
8. Oil output increased.
9. Lower cost of repairs, maintenance and production.
10. Dust and smoke nuisance suppressed.
11. Elasticity of operation.
12. Capability of producing a new superior quality of patent fuel for metallurgical, industrial and domestic purposes.

#### SPECIAL TREATMENT OF BITUMINOUS COALS BY THE PIETERS PROCESS

As to the question how to treat at its greatest advantage the bituminous coals from your districts, having from 33 to 42 per cent of volatile matter, 8 to 14 per cent of ash and 2 to 7 per cent of sulphur; an economical treatment in any of the ordinary coke oven systems or in any of the present known gas retorts, is not possible as none of them are capable of obtaining from these bituminous coals—very rich in gas—the greatest part of their value. On one hand, the coke obtained will be too much swollen, having very little resistance, quite inadequate for metallurgical purposes, or even for domestic requirements; while on the other, the actual process of high temperature distillation gives but a relatively low yield of tar products, caused by the pyrogenation of the oils at a high temperature. The ammonia also undergoes decomposition in the presence of the carbon, producing cyanogen, which is very detrimental to the conservation of the apparatus and piping of the by-product works.

My new process of distillation not only increases the value of the coke by producing a quite new combustible having all the qualities of metallurgical coke, but it also increases the yield of oils, benzol, ammonia and gas surplus in very large proportions.

Before carbonizing, the coal is agglomerated into ovoids or briquettes, the dimensions of which depend solely on the destination of the new fuel. The agglomeration is done by any known process, the coal having been mixed with a very small proportion of pitch. (If required the coal dust can be washed beforehand so as to reduce its ash and sulphur percentages to the most convenient limit.)

The agglomerates so obtained are charged directly in the oven together with a certain quantity of a certain substance suitably pulverized. This substance suitably mixed with the agglomerates not only prevents any deformation during distillation, but also allows a very regular carbonization of each and every one of the agglomerates.

The distillation takes place in a very slow and progressive manner, at first at a very low temperature then gradually increasing during the advancement of the agglomerates down the oven to a final temperature of about 1742°F. which corresponds to its complete coke formation.

The volatile products free themselves slowly and are directly drawn off in such a way that it is impossible to obtain any overheating of them or clogging of the apertures. The pitch used for the manufacture of the agglomerates is cracked during the distillation, only about 10 per cent remaining as carbon, constituting the first cementing together of the coal particles, while about 50 per cent of it is converted into light, middle and heavy oils of a superior commercial value to the pitch itself. The balance is returned as non condensable gas.

After the carbonization is completed, the coke obtained undergoes a gradual and complete cooling process in the lower part of the oven as explained before.

On account of this recovery of nearly all the heat in the coke, which is returned afresh to the oven, the economy in firing is very important. To this economy the smaller loss of heat by radiation and in the products of distillation has to be added; the result is a total economy of about two-thirds of the quantity of gas actually used for firing purposes in the ordinary coke-ovens.

Outside the increased yield in tar oils, ammonia, benzol and available gas, the most important advantage of my process consists in the far superior quality of the coke produced. This coke presents itself in regular lumps, all of the same size, very resistant, hard, dense and of a very high combustibility. It can be stocked indefinitely without producing any waste.

Notwithstanding the cost of the supplementary installation for the agglomerates, the total cost of a complete installation of this new process is less than the cost of a complete battery of ordinary coke-ovens, quantity for quantity, but its operation expenses are much less on account of an important reduction in manual labor and the total suppression of water consumption.

The increased yield of manufactured products per ton of coal will be as follows:

1. An increase of 3 gallons of tar oils.
2. An increase of at least 4.5 pounds of sulphate of ammonia.
3. An increase of 0.5 gallon of benzol.

4. An increase of at least 2293 cubic feet of gas of 546 B.t.u.
5. A much more important net coke yield having a greater value.

Besides the superior quality of the coke product the financial economies secured by treating these coals in this oven, in comparison with the ordinary oven can already safely be estimated to represent at least \$2.00 per ton of coal treated, representing a supplementary profit per annum equal to about 50 per cent of the cost of the installation.

If we take as a typical average quality of your bituminous coal, a coal containing 37 per cent of volatile matter, 4 per cent moisture and 12 per cent ash, with a tar output by low temperature distillation (Fischer's retort) of 27.5 gallons; the products, which you will be able to obtain by my new carbonization process will approximately be per ton of 20 cwt.:

<i>Benzol and Motor spirit</i> .....	3 gallons
<i>Diesel oils</i> .....	5 gallons
<i>Fuel oils</i> .....	11 gallons
<i>Phenols</i> .....	4 gallons
<i>Sulphate of ammonia</i> .....	24 pounds
<i>Gas surplus</i> .....	7000 cubic feet of 546 B.t.u.

Coke of a definite size: 12 cwt. which can be used either for metallurgical purposes, for domestic and industrial purposes, or in gas producers (see Fig. 6).

The above results will compare most favorably from all points of view, and especially from a commercial and economical one, with those which you would obtain from any other process.

The best process of transformation of a combustible will always be the one which will produce one or more new products of a superior industrial value at a very low cost of production. The reduction in cost depends to a large extent upon the utilization of a very small quantity of calorific energy.

Transformation operations always had to be based on the principle that the useful calorific value of the new manufactured fuel is not inferior to the calorific value of the initial combustible, otherwise transformation would result in destruction instead of conservation of the actual reserves. The Iron Age depends for its continuance upon the supply of adequate fuel. The quicker the fuel reserves are destroyed the sooner will the Iron Age pass away.

# EXTRACTION AND RECOVERY OF PHENOLS FROM AMMONIA LIQUOR

By ROBERT M. CRAWFORD

*Chemical and Industrial Engineer, Pittsburgh, Pennsylvania*

Waste liquors from coke-plant ammonia stills constitute a recognized source of stream pollution due to the presence of phenols which are scrubbed out of the gas by the flushing liquor and which ultimately reach neighboring streams via the ammonia still waste liquor.

The phenols exist in the "free" state in the crude ammonia liquor but in the presence of lime, which is added to the liquor to decompose the "fixed" ammonia, the phenols are "fixed" in the form of calcium compounds. However, due to the absorption of carbon dioxide from the atmosphere, or to free acids in the stream into which the still waste is discharged, the calcium compounds of the phenols are decomposed, thus liberating the phenols in the free state,—perhaps a considerable distance away from the offending plant,—stream pollution resulting.

The purpose of this paper is to discuss broadly the Solvent Extraction Method for the substantial elimination of phenols from ammonia liquor and their recovery as a salable by-product in the form of Crude Tar Acids.

The free phenols in crude ammonia liquor are efficiently extracted with solvents (such as benzol, motor-fuel or coal-tar light oils); are readily removed from the solvent extract by passing the extract through a solution of caustic soda and the phenols recovered in salable form by neutralization of the phenolate formed by the caustic soda solution. Briefly stated, these steps constitute the method under discussion and at least four operating installations testify to the successful commercial application of these successive process steps.

## EXTRACTION OF LIQUOR

The principle underlying the extraction of phenols from the liquor is given in the Law of Berthelot which states that when two immiscible solvents are simultaneously in contact with a substance soluble in both, the substance distributes itself between the two solvents so that the ratio of the concentrations reached in both solvents is a constant (equilibrium is of course assumed).

Thus, if a quantity  $P_0$  of the substance (phenols) exists in a quantity  $L$  of the first solvent (liquor), and this solution be extracted with a quantity  $S$  of the second solvent (benzol, or motor-fuel) and there remains a quantity  $P_1$  in the first solution, then a quantity  $P_0 - P_1$  has passed into the second solvent. The value, then, of the quantity  $P_1$  is, in accordance with Berthelot's Law, given by the following equation:

$$(1) \quad \frac{P_1}{L} = K \frac{P_0 - P_1}{S}$$

or

$$(2) \quad P_1 = P_0 \frac{KL}{S + KL}$$

since  $\frac{P_1}{L}$  and  $\frac{P_0 - P_1}{S}$  are two concentrations after equilibrium has been established and  $K$  is the constant, or what is commonly called the "Partition Ratio," or "Distribution Coefficient."

To follow further, a second extraction with the same quantity  $S$  of the second solvent gives:

$$\frac{P_2}{L} = K \frac{P_1 - P_2}{S}$$

and substituting the value of  $P_1$  from equation (2):

$$(3) \quad P_2 = P_0 \left( \frac{KL}{S + KL} \right)^2$$

and for the  $n$ th extraction:

$$(4) \quad P_n = P_0 \left( \frac{KL}{S + KL} \right)^n$$

$P_n$ , the quantity of the substance (phenols) remaining in the first solvent  $L$  (liquor) diminishes as  $n$  increases, as  $S$  (solvent) is greater and as  $K$  (partition ratio) is less. Complete extraction is not possible because  $\left( \frac{KL}{S + KL} \right)^n$  can never become zero; it can approach zero, however, and an extraction efficiency satisfactory for practical purposes can be attained.

It can be shown by the use of higher mathematics that, with a given quantity of the second solvent ( $S$ ), a more complete extraction

can be effected by extracting frequently with small portions of the solvent than by using larger quantities a correspondingly less number of times; a procedure known to every chemist.

In actual practice the above principles are applied with, a constant ratio of liquor ( $L$ ) to solvent ( $S$ ) at about 1:1.2, and an attempt to make  $n$  infinitely great by dispersing the solvent into the liquor in continuous, counter-current flow; which combination makes for high extraction efficiency in continuous fashion with the least amount of solvent.

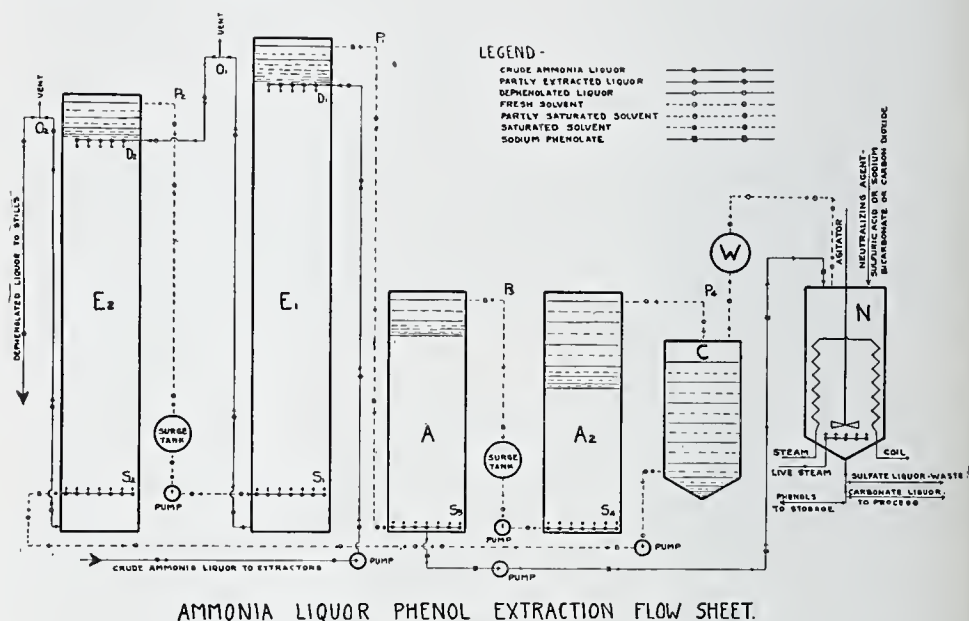


FIG. 1

The following is descriptive of a typical installation (refer to Fig. 1):

The crude liquor is pumped continuously to an extraction tower ( $E_1$ ) through a distribution manifold ( $D_1$ ) located at a point near the top of the tower and is distributed uniformly over the cross-section of the tower. The level of liquor in the tower is maintained preferably at the distributor manifold level ( $D_1$ ) by means of an adjustable siphon overflow ( $O_1$ ). The liquor flows continuously downwards in the extractor ( $E_1$ ) and overflows into a second, shorter, but similar extractor ( $E_2$ ), being entered at the distributor manifold ( $D_2$ ), flows downwards, and leaves at the siphon overflow ( $O_2$ ), which maintains the liquor level in the second extractor ( $E_2$ ) at the distributor manifold level ( $D_2$ ) as in the first extractor ( $E_1$ ). The second extractor

( $E_2$ ) is a few feet shorter than the first extractor ( $E_1$ ) in order to provide sufficient static head of liquor to produce proper flow.

Counter-current to the flow of the liquor in the extractors, ( $E_1$ ) and ( $E_2$ ), is a flow of solvent (usually motor-fuel, or more lately unwashed coke-plant light oil) which is pumped from a circulating tank ( $C$ ). The solvent is first dispersed into the bottom of the second extractor ( $E_2$ ) by a distributor manifold ( $S_2$ ), located a few feet from the bottom of the extractor. The dispersed solvent, in the form of small globules, spread uniformly over the cross-section of the extractor, rises counter-current to the downward flow of liquor, extracting the phenols, and collects as a supernatant layer of partially saturated solvent on top of the liquor. The extract then overflows at ( $P_2$ ) to a surge tank, from which it is pumped to the solvent distributor manifold ( $S_1$ ) of the first extractor ( $E_1$ ) in which it performs a similar extraction, collects as a supernatant layer of strong extract and overflows at ( $P_1$ ) to the caustic soda absorbers.

Extraction efficiencies average about 94 per cent on normal operation with a solvent to liquor ratio of 1.2:1 with approximately 70 per cent extraction taking place in the extractor ( $E_1$ ).

The capacity of a set of such continuous extractors is obviously a function of the area of the towers, while the extraction efficiency is a function of the height of the towers (contact time), other things being equal. In present practice the height of the towers are about 37 feet and 35 feet respectively.

The dephenolated liquor leaving the extractors passes to the ammonia stills and contains some solvent in solution. This dissolved solvent is, however, fully recovered since it is driven into the gas stream with the ammonia gas from the ammonia stills, passes with the gas through the saturators and final coolers, is absorbed in the benzol scrubbers, and is finally recovered along with the normal light oil yield which it augments.

#### CAUSTIC ABSORPTION

The strong solvent extract of phenols overflowing from the extractor ( $E_1$ ) is dispersed into a solution of caustic soda (20 to 23 per cent) contained in two caustic soda absorbers ( $A_1 - A_2$ ). The solvent extract first passes through the alkaline solution in the first absorber ( $A_1$ ), gives up phenol, which reacts with the caustic soda to form sodium phenolate, and partially dephenolated solvent collects on top of the solution as a supernatant layer. It overflows at

( $P_3$ ) into a similar, absorber ( $A_2$ ) giving up the balance of the phenols, collects again as a supernatant layer of dephenolated solvent and overflows at ( $P_4$ ) into the solvent circulating tank ( $C$ ) to be recycled through the liquor extractors.

When the caustic soda solution in the first absorber ( $A_1$ ) has become saturated with phenols, the phenolate is pumped out for treatment, the partly saturated soda solution in the second absorber ( $A_2$ ) transferred to the first absorber ( $A_1$ ) and a charge of fresh caustic soda then put in the second absorber ( $A_2$ ). During this transfer suitable provisions are made not to interrupt the extraction cycle.

#### PURIFICATION OF PHENOLATE

The sodium phenolate solution collected from the first caustic absorber ( $A_1$ ) contains impurities in the form of solvent, tar oils and naphthalene, which must be removed before the phenolate is acidified to recover the phenols in the free state. These steps are accomplished in the vessel ( $N$ ).

The crude phenolate is pumped into the vessel ( $N$ ) and heated by means of steam coils, the dissolved solvent vaporized, condensed in the condenser ( $W$ ) and the recovered solvent returned to the solvent circulating tank ( $C$ ).

Next the phenolate is steam distilled with live steam, thus removing the tar oils and naphthalene. These vapors are either condensed or blown into the air.

#### NEUTRALIZATION OF PHENOLATE

The purified phenolate is next acidified in the vessel ( $N$ ) either by the addition of sulfuric acid or crude sodium bi-carbonate.

Where sulfuric acid is used it is customary to add 60 Be acid slowly to the cooled phenolate, with agitation either by air or a mechanical agitator. When the reaction is complete (slightly acid to litmus paper), the products separate, on standing, into an upper layer of free phenols and a lower layer of sodium sulfate solution. The lower layer is separated off, discarded, and the phenol layer sent to storage.

At one of the operating installations it has been found desirable to neutralize the phenolate by the addition of crude sodium bicarbonate, which is sufficiently acid to effect the decomposition of the phenolate. By this method, a warm paste of sodium bi-carbonate is made with water, added to hot phenolate with agitation and after the neutralization is complete, the products are separated as before.

On neutralization of phenolate by sodium bi-carbonate, the spent liquor formed is a solution of sodium carbonate and at this plant the carbonate solution is used to desulfurize coke-oven gas in a Koppers Liquid Purification Unit, which accounts for this rather odd method of neutralization.

#### CHARACTERISTICS OF PHENOLS RECOVERED

The phenols recovered by the process are presented in the form of a reddish brown liquid having a specific gravity of about 1.05 (30C) containing water varying from 2 to 12 per cent depending upon how much dehydration has been effected in the process.

On a dry basis, the composition of the product is somewhat as follows:

	<i>per cent</i>
Phenol.....	57
o-cresol.....	13
m-cresol.....	8
p-cresol.....	10
Higher acids and residue.....	12

#### PROPOSED IMPROVEMENTS

As a result of several years experience in the commercial application of the Solvent Extraction System, certain logical improvements, which appear to offer lowered installation and operating costs, suggest themselves. (Refer to Fig. 2.)

In the Extraction and Absorption steps it would appear that the two towers used for each step could be combined into single towers having a cross-section area equal to the total area of the two towers and having a vertical partition serve to separate the single towers into two vertical compartments of semi-circular cross-section. Each compartment would thus function as a separate Extractor or Absorber. Such a set of towers would be much cheaper to build and erect, thus reducing the cost of installation.

It would appear reasonable to regenerate caustic soda by neutralizing the phenolate with gases containing  $\text{CO}_2$  and then to causticize the sodium carbonate liquor thus generated by the addition of lime in accordance with common practice in the recovery of tar acids from tar oils.

To accomplish caustic regeneration one could circulate the phenolate through a small absorption tower (*R*) against an ascending flow

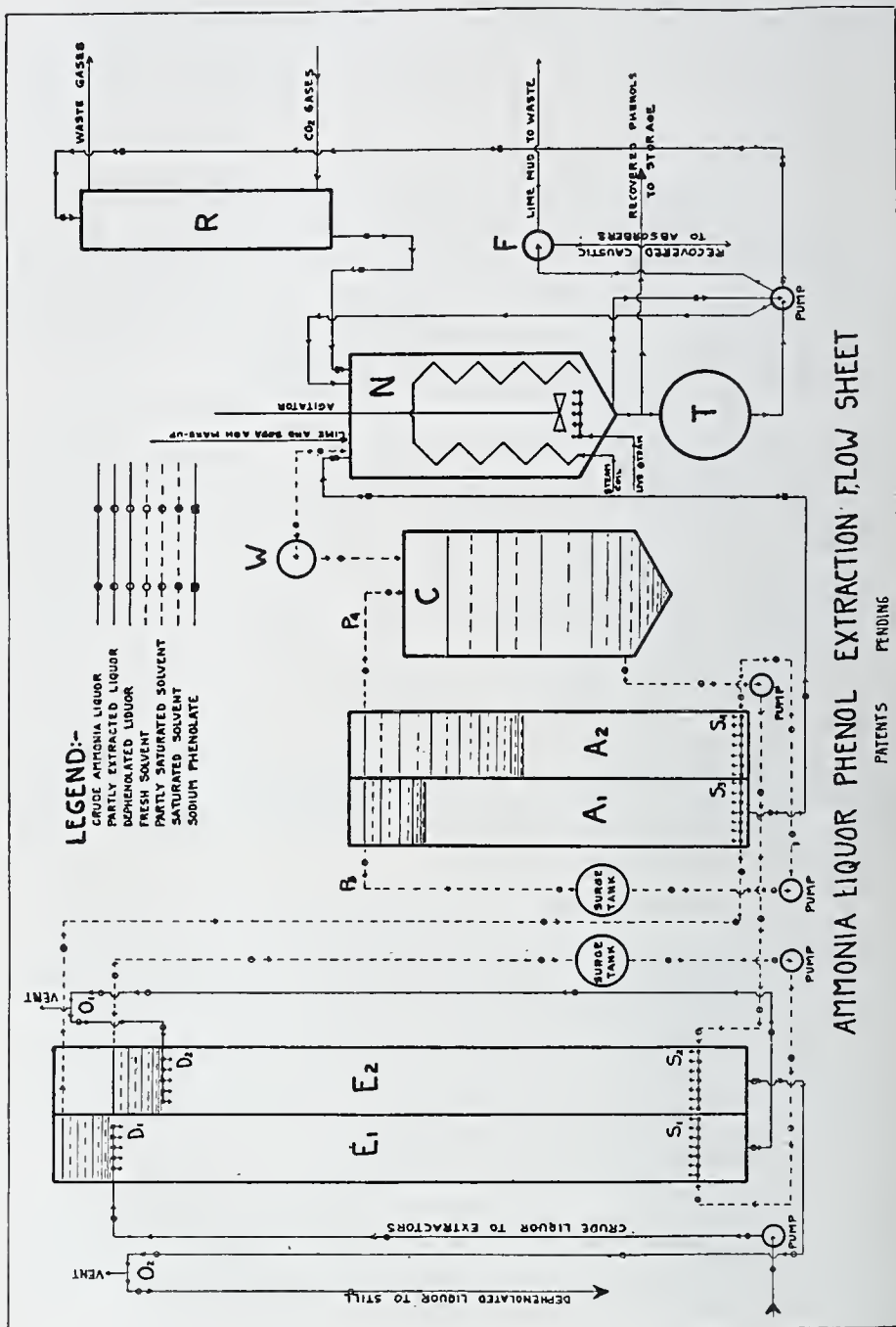


FIG. 2

of gases containing  $\text{CO}_2$ , generated, say, by the decomposition of limestone with coke or gas. After neutralization the lower solution of sodium carbonate could be separated into a rundown tank (*T*), the phenols sent to storage and the carbonate liquor then returned to the vessel (*N*) to be causticized by the addition of lime. After causticizing the "lime mud" could be filtered out in a filter (*F*) and the regenerated caustic reused in the caustic absorbers. To make up for caustic losses, which necessarily accompany such an operation,

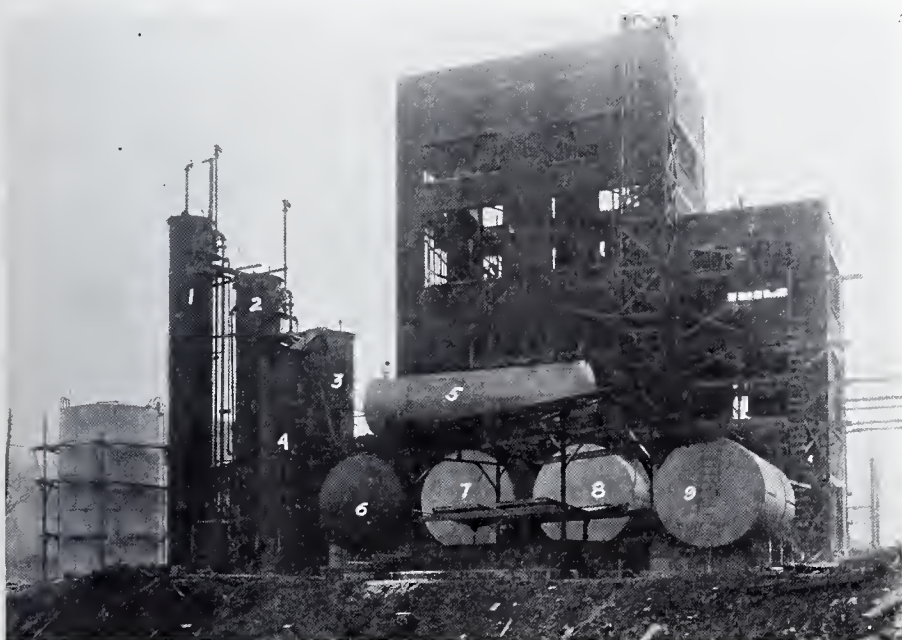


FIG. 3

some make-up soda ash (together with its lime equivalent) would need to be added on causticizing.

#### CONCLUSION

Figure 3 is a photograph of the installation mentioned as operating with crude sodium bi-carbonate as the neutralizing agent. 1 is the first liquor extractor; 2 is the second liquor extractor; 3 is the first caustic absorber; 4 is the second caustic absorber; 5 is the steam still and neutralizing tank; 6 is the solvent circulating tank; 7 is the carbonate liquor storage tank; 8 is the phenol storage tank; 9 is the caustic soda storage tank.

## DISCUSSION

JOSEPH D. DAVIS: I have for a long time considered the carbonized briquette an excellent fuel. It is uniform in size, dense and resists shock well during handling. The method has the advantage that a coked fuel can be made from raw material that ordinarily will not coke—that is, by mixing with binder and briquetting. I see no reason against using such a fuel in a cupola or blast furnace, but do not know of instances where this has been tried. I would certainly not like to have to decide without trial what a new fuel is going to do in a blast furnace because even with cokes made in the usual way there are differences in blast furnace behavior which cannot be accounted for by variation in properties as shown by the usual chemical and physical tests. I do not think that enough carbonized briquettes have been made in this country for conclusive blast furnace trial and we do not know what the result would be. However it seems to me that the carbonized briquette has uniformity of size and quality decidedly in its favor.

Compression of the charge during coking, it will doubtless be agreed, improves coke density and broadens the field of coals available for carbonization. It aids in the agglomeration of weakly coking coals. From known failures of attempts to work out this method technically, one gathers that it is a difficult problem, particularly where the process is continuous. If Mr. Pieters has solved this phase of the general problem he is certainly to be congratulated.

If the statement that “the phenomenon of coal distillation . . . produces an enormous amount of heat” means that the reaction heats are strongly exothermic, I cannot agree. The reaction heat, if positive at all, is small and it does run negative in many cases.

MR. CRAWFORD (Referring to Pieters' paper): I have just made a rough heat balance from this table, taking the approximate calorific value of the motor spirit and the tar and gas and the coke. The figures show an almost 100 per cent heat balance, which you do not expect. You have some losses in carbonization.

For instance, I have taken 27,000,000 B.t.u. in an average ton of coal and the total proximate heat value of these products give, from the table, a total of 26,691,000. It does not seem feasible. He does not say that these are steamed at all, does he?

DR. JAMES: No. That is an externally heated retort.

MR. CRAWFORD: The ammonia used was very high, 27 pounds of sulphate.

# LONG DISTANCE TRANSMISSION OF COKE OVEN GAS IN GERMANY

By DR. ALFRED POTT

*General Director, Ruhrgas Aktiengesellschaft Essen am der Ruhr, Essen*

*Read by Dr. Wilhelm Raelen, Director of Mines, United States Steel Company*

In the fall of 1926 about 90 per cent of the coal mines of the Rhenish Westphalian Coal Syndicate formed the Coal Exploitation Corporation, now called the Ruhrgas Corporation. Its purpose was to develop the chemical processes of coal refinement such as hydration of coal, production of synthetic ammonia using coke oven gas as source of hydrogen, low-temperature carbonization of coal, the combustion of powdered coal and the building up of a large scale gas distribution system, with the Rhenish Westphalian industrial district as the bases.

At the beginning of the work it was found very soon that the completion of the long distance gas supply system was the most urgent. Furthermore, all essential technical problems for carrying out this project had been largely solved or their solution could be expected in the near future. For this reason it was possible to proceed immediately with this project.

The purpose of my address is to acquaint you with the underlying technical and commercial principles of this enterprise, dwelling particularly on such technical details as developed during the work of the last year and a half as being of special importance.

In order better to explain to you the economic background of the proposed long distance gas distribution I will draw a comparison with conditions in the United States.

In the drilling for oil, large volumes of natural gas were obtained for which, in most cases, there was no local market. If these valuable resources provided by nature were not to be wasted, it was necessary to transport the gas through pressure lines over hundreds of miles to points of economical utilization. These circumstances have made the United States the leader in long distance gas distribution.

It was for similar reasons that the enterprise for long distance gas distribution was organized in the Rhenish Westphalian industrial region. As the natural gas is piped from the oil and gas fields to dis-

tant communities, so in Germany the excessive coke oven gas will be piped from the coke plants through long lines to distant points for more economical utilization.

One hundred and twenty million tons of coal were mined in the Ruhr district in 1927 and about twenty-seven million tons of coke were produced. This coke production is the equivalent of about ten billion cubic meters of gas. Of these quantities of gas we have been using 45 per cent for heating the coke ovens and about 45 per cent as fuel for the steam plants at the mines. Only the small balance of 10 per cent was supplied for outside uses; namely, for the generation of electric power and for lighting of municipalities, and for metallurgical purposes.

The use of valuable coke oven gas for the generation of steam at the mines and for the heating of coke ovens must today be considered uneconomical, since for this purpose, especially at times when business is slack, sufficient quantities of low grade fuel, such as middlings from coal washing plants, coke breeze, or other unsalable grades are available, which due to the recent developments in fuel and combustion engineering and of new types of coke ovens can be utilized with a high degree of efficiency. These circumstances favor the use of low grade solid fuels at the mines thereby saving the highest grade fuel which the mining industry possesses, namely, the coke oven gas, for purposes where its full value may be realized.

The conditions in other German mining sections are quite similar to those in the Ruhr district so that there, too, the problem of gas distribution is being seriously considered. The geographical distribution of the individual German coal fields is extremely favorable for the realization of the ultimate plan which has as its aim to offer the most economical supply of gas to as many parts of the country as possible. Primarily, the scheme visualizes main lines extending from the various coal centers in all directions where the distribution of gas promises to be a lucrative proposition. Glancing over the map it can easily be ascertained where the main pipe lines of the various mining companies have to meet, so that by connecting them a complete network of distribution is formed. The coöperation of the various companies that is then made possible is a valuable safeguard against interruption of distribution in case of emergency.

The all important question was, what pressure conditions should exist in an overland gas distribution of such proportions? That is, what pressures and pipe diameters must be used in order to make the transport of gas as economical as possible?

This question cannot be answered in a general way. The respective local and technical conditions have to be taken into consideration. Special attention has to be paid to two important factors: first, the pressure which can be used, based on the present status of pipe line engineering and on the quantity of gas and distance; and second, the influence of the pressure on the composition of the gas, as well as on the safety of the gas transport.

The principal items of the cost of gas distribution are the interest on capital investment, the operating cost of pipe lines, compressor plant and measuring equipment and also the losses of gas.

For the transportation of a certain quantity of gas over a certain distance, these costs converted into pfennigs per cubic meter or cents per cubic foot, will vary depending on the selection of pipe diameter and the relative initial pressure which is determined by it in conjunction with the quantity and distance. In order to eliminate the rather extensive calculations to determine the economical diameters and starting pressures for each case, we have endeavored to calculate in a general way, the variation of the economical diameter in relation to the increase of quantities and distances, based on conditions prevailing in Germany. We have succeeded in charting the results in a rather simple form so that for each rate of gas flow and for each distance, the most economical diameter and the initial line pressure determined by these factors may be read. These tables have confirmed again the long-known fact that the transport of large quantities of gas at shorter distances is most economical by use of large diameter pipe lines at a low pressure. If it is desired to convey the same quantity of gas over a longer distance, smaller diameters and higher pressures should be used. By applying the curves shown on the charts to the conditions underlying the present project, the initial pressures up to 30 atmospheres and pipe diameters of about 500 mm. (20 inches) were found to be required.

A special condition exists in the Ruhr district which had to be considered. A large quantity of the available gas will be used in close proximity to its point of origin in the Rhenish Westphalian industrial district itself. Here are numerous industries for which, according to past experience, the introduction of gaseous fuel has been found to be particularly desirable and which, by the nature of things, would have a large consumption of gas. It would be uneconomical to compress the gas immediately to a very high initial pressure and have it available at an unnecessarily high pressure within the distance of sixty

to seventy kilometers. If we take further into consideration that the Rhenish Westphalian industrial district with its numerous mines located in close proximity to each other (there are 358 mines within an area of 1,200 square kilometers) is subject to considerable underground earth movements, this feature would also make a low initial pressure very desirable.

After having considered fully all the advantages and disadvantages an initial line pressure of from 3 to 6 atmospheres (about 45 to 90 pounds) was decided upon.

The lines are sufficiently large to transport the amount of gas required over a distance of 90 to 100 kilometers, even under the assumption of the highest available volume of gas. If in the course of development it should prove necessary to convey large quantities still further, provision has been made to install additional intermediate compressor stations at a distance of 60 to 70 kilometers at points where the consumption of large gas quantities has already taken place due to the industries. It has been taken into consideration that the gas pressure should not be completely released, since through applying a suction pressure of 1 to 2 atmospheres, the cost of the intermediate compression can be considerably reduced. The new initial line pressure will then amount to 12 and up to a maximum of 20 atmospheres. At these pressures the lines call for a diameter of 700 mm. and down to 400 mm. (28 inches down to 16 inches).

This solution can of course not be generalized. For instance, next year a line of 200 kilometer lengths is to be built where the gas is immediately compressed to the required pressure of 12 atmospheres (175 pounds).

What influence does this relatively high pressure have on the composition of the gas, and do we have to figure on condensation of gas constituents?

This question came up when the very first long distance gas lines were laid in Europe. At that time extensive tests were made to determine the influence which the pressure has upon the luminosity which at that time was still an important characteristic of gases. The results varied depending on the length of the line and according to the season during which the tests were made. Since then conditions have changed. The candle power is no longer an important quality of the gas, and the main illuminants in the gas, the hydrocarbons such as benzol, xylol and their homologues are now extracted from the gas, by the most economical methods, at the points of origin and especially at the coke plants.

When the large project for long distance transmission of gas throughout Germany became assured, additional detailed investigations were nevertheless made to determine if it was necessary to reckon on a condensation of heavy hydrocarbons, (about the composition of which very little is known so far), due to the high pressures which are to be employed in the transportation of the gas over such long distances. These tests were made by Professor Bunte of the Gas Institute at Karlsruhe. A mixture of hydrocarbons was frozen out of coal gas and the boiling points of the individual fractions were determined. In comparing these boiling points with the boiling points of various compounds which are found in coal tars and therefore, under certain conditions, in illuminating gas, it was found that these elements in illuminating gas only exist in concentration which will not produce condensation at 30 atmospheres or above.

A questionnaire sent to the existing gas distributing companies in Germany has shown that in cases where condensation could be observed it consisted mainly of water, oil and naphthalene. Furthermore, this oil is not composed of the elements of the illuminating gas but, according to an analytical investigation, represents compressor oil which was carried along by the gases heated by compression and was condensed out in the colder sections of the pipe line. Therefore as far as condensation is concerned there should be no fear or hesitancy as to the application of high initial line pressures.

On the other hand the influence of the pressure on the separation of possible quantities of naphthalene contained in the gas is much more serious. The difficulties are well known which most of the gas plants suffer through the naphthalene depositing in a fine, laminated form which sticks to the pipe and causes any line, no matter how large, to become completely clogged within a short time. The higher the pressure under which the gas is kept the more naphthalene will naturally be deposited. In spite of this, experience so far has shown that with higher pressures troubles due to deposit of naphthalene occur much less frequently than at lower pressures. Investigation on existing long distance gas lines have shown that the naphthalene at higher pressures separates out in an entirely different form than at lower pressures, not in a laminated deposition but partly as a solid crust on the pipe walls and partly dissolved in the compressor oil which was carried along by the gas. Above certain pressures, as can readily be understood, the precipitation of the naphthalene takes place only in this solution in oil and can be removed from the line without difficulty through the water seals.

In order to remove all uncertainties in this regard and to secure the safe delivery of gas free from all possibilities of trouble, a process has been developed to be used in connection with this long distance gas project for the complete removal of naphthalene from the gas. This will be discussed more fully in connection with the proposed installation of coke plants.

How does present pipe line engineering measure up to the demands of a high pressure system such as this?

As long as nothing better than couplings packed by tar rope, lead wool, asbestos or rubber bell and spigot joints were available for the laying of pipe lines, the application of such high pressures was hardly possible. The gas losses which of course increase with the age of the line endanger both the safety and economy of the gas transport. A serious consideration is also the danger caused by leaks and subsequent infiltration of gases into dwellings. This feature requires particular attention in cases where the lines go through densely populated regions such as is the case with the lines that are now being built.

Since we now possess a material, which, thanks to the successful development of modern welding practice, can be joined by gas and electric welding, no difficulties confront us in the construction of long distance gas lines even on the largest scale. The problem of pipe line construction even for the highest pressures may today be considered as being completely solved.

The material most suited for high pressure lines is steel having a tensile strength of 34 to 41 kgm. per square millimeter (38,000 to 58,000 pounds per square inch) and an elongation of more than 25 per cent.

The use of a harder steel is generally not advisable in view of the imperfections of the welding seam. The steel tubes of largest diameter are furnished by the German tube companies in water gas welded pipe (from 300 mm. (12 inches) up to the largest diameters) below these sizes seamless tubing is employed (from the smallest diameter up to 500 mm. (20 inches). The length of the seamless tubes is 13 to 16 m. (42 to 50 feet) and the length of the water gas welded tubes is 8 m. (about 25 feet). For the construction of long lines it is preferable, in case water gas welded pipes are used, to weld two pieces together at the mill so that lengths of 16 m. (about 50 feet) are available. By that means, the number of welds in the field is reduced to one half, inasmuch as welding in the field requires

more time than it does in the mill and a considerable time saving is attained.

One of the primary requirements for the construction of a good pipe line is a first class welding crew. In order to have assurance in this respect, only welders should be employed in the construction of high pressure lines who have received their training in the numerous well equipped welding schools or institutions of that kind.

The question whether gas or electric welding should be employed cannot be answered offhand. Judging from the results of investigations up to date there should be no difference in the quality of the welded seams. Such differences, if existing, are considerably smaller than those which result from more or less personal fitness or skill of the welders.

For the welded connections of individual pipe lengths, many schemes have been prepared during recent years. It is necessary to find a connection which is very simple to weld and which has a great elasticity against the forces acting both vertically and longitudinally in relation to the axis of the pipe and where the welding seam itself is not affected by these forces. Since the question of couplings for a high pressure pipe line is of the highest importance, numerous tests have been made along this line before starting actual construction. The results have shown that one coupling, the so-called "Kloepper" coupling, above all others possesses all the above-mentioned characteristics in the highest degree. In the construction of the new line this coupling is being used to a great extent and is especially preferred in districts where movement of the subsoil is to be feared as in the mining districts, at railway and main road crossings.

Of special value is also the so-called ball coupling which in principle is identical with the "Kloepper" design, only the couplings and tube ends are so designed that the tubes can be welded together at an angle. This coupling enables us to change the direction of the line up to  $6^{\circ}$  without the use of special elbows.

The laying of the line is generally at a depth of about 80 cm. (about 32 inches) which is sufficient in Germany to protect the pipe line against excessive fluctuations in the temperatures. Nevertheless the use of expansion couplings could not be entirely eliminated, especially near gate valves and in mining regions.

Obstacles for pipe lines due to conditions or contour of the ground exist no longer on account of the extensive experience which has been accumulated in the building of pipe line supports, ducts or bridges

and tunnels; one of these ducts was laid across the Rhine as early as 1917 with a length of 501.9 m. (airline), representing thereby the largest crossing in a running stream in Europe. Since this duct has been in use, no troubles of any kind have occurred.

Much more serious, in number at least, are the difficulties encountered in the laying of long high pressure lines in densely populated regions, due to the many unavoidable crossings of highways and railroads. Due to the densely built up railroad network in Germany the pressure lines must cut across railroad lines very frequently which has made it necessary to work out methods whereby the crossing of a railroad can be accomplished in the quickest possible manner without disturbing the railroad traffic. One method is very interesting by which a protecting outer pipe is pressed through the railroad dam by means of a hydraulic press. A man loosens the earth in the front end of the pipe and conveys it to the outside in small cars. The actual pipe is then shoved into the protecting pipe by means of small sleds.

The laying of pipe lines in Germany can, in most cases, only be done on highways and streets. Although this is favorable for the delivery of the materials, the actual work of laying becomes much more difficult since the majority of the streets are crowded with pipe lines, cables and street car tracks. For this reason the use of trench diggers so highly developed in the United States cannot be considered. The digging of pipe trenches has to be done by hand, and with the greatest possible care. Furthermore, the maintenance of traffic during the construction work has to be fully considered.

On account of these special road conditions the laying of lines is done as follows: The tubes assembled to make up the right length of the line are laid out upon supports about 1 m. (3 feet) high and there welded together in sections about 100 m. (300 feet) in length. After closing the two ends of this section of the line by means of covers, it is then put under pressure, the pressure equaling the final operating pressure of the line. The welded joints can very easily be checked for leaks by soaping them. Meanwhile the pipe trench has been dug out underneath the supports of the pipe strand and the strand of about 100 m. is then lowered uniformly into the trench by means of cranes of special design mounted on trucks.

The method has the following advantage: only a narrow strip of the road is temporarily blocked against traffic. Sixty per cent of the welding can be done outside of the pipe trench and therefore

in considerably less time than would be possible in the trench itself. The expensive digging of coupling holes is completely eliminated. More rapid laying of the line at a lower cost is the natural result.

In order to be able to test the tightness of connections welded within the pipe trench, greater lengths between two valves or representing an average distance of 2 to 3 kilometers are afterwards re-tested under the regular operating pressure. This enables a thorough check on all welding resulting in the greatest safeguard for a pipe line of the best quality.

A very essential factor in the durability and safety of operation of the line is its protection against corrosion. This is usually taken care of by a special pipe insulation consisting generally of a jute-like cloth covering, and a layer of an insulating material. The cloth covering usually consists of impregnated jute, or wool felt is used. The best insulator has proved to be natural bitumen as it does not harden or become brittle as is the case with many other insulating materials. The quality of being leak-proof and acid-proof, so important in insulating materials, are retained for a long time. The insulation of the pipes with the exception of the couplings is done mechanically in the tube mills where uniform and careful workmanship is guaranteed. The shipment of the insulated pipes must of course be handled with very great care; it is further advisable not to expose the pipe too soon in the laying of strands so as to avoid damaging the insulating material. Should this happen, which is only a rare occurrence, then the insulation must be mended at the same time the welded joints are insulated before lowering the pipes into the trenches. It is of great importance to safeguard properly the line against electric currents in the ground. Recently objections have been raised against the flange insulations which formerly were often used because in most cases the insulator consists of soft para rubber which is subjected to the influence of the gas. Inasmuch as caoutchouc (india rubber) is soluble in hydrocarbons and furthermore since small quantities of organic sulphur are continually absorbed from the gas, a hardening and embrittlement of such connections could hardly be avoided. On the other hand, the method of indirect protection against earth currents through electric counter action is becoming more and more important. It is not possible to establish general guiding principles for this application since the strength of currents as well as the character of the ground demand different treatment. For the time being

the best system is to avoid ground currents by proper provision at the power plants and the permanent supervision through measurement of the intensity of the current at the points in question.

The above described method of laying pipe lines is generally being employed in the installation of the pipe lines for the long distance gas distributing system from the industrial district.

By the end of 1929 about 650 kilometers of lines will have been laid. The Ruhrgas Corporation has acquired by purchase the existing system of the Rhenish Westphalian Power Corporation, consisting of lines totaling 300 kilometers in length and covering a district of about 766.5 square kilometers and by the end of the year 1929 a network of pipe lines altogether 950 kilometers in length will be available to bring the excess gas production of the coke plants to economical use. Through this system a territory of about 11,000 square kilometers, having a population of about ten million people can be supplied with gas. The gas supplied through these lines will by the end of the coming year amount to about two billion cubic meters annually.

This pipe line system will receive its supply of gas from the individual coal mines of the Ruhr district.

In the beginning of this project we had to figure with connections to about 125 individual mines. Since fall 1926, however, the conditions have changed considerably since the coke industry of the Ruhr mines in the midst of a rationalization and modernization of its plants on a large scale. The numerous coke plants of individual mines with an annual production of 100,000 tons of coke each were considered antiquated. New coke plants had to be built. The modern construction of coal mixing plants and the continuous progress in mechanization means of coke plant operation, have made it possible to concentrate the production of coke in a large central coke plant supplied with coal from several mines. For this reason only 45 new coke plants of 260 ovens or over need now to be connected to the long distance gas system, having a daily capacity of up to 4000 tons of coal; it must be kept in mind that the oven chambers have increased in size much more than in numbers, since chambers up to 6 mm. high and 13 mm. long can today be uniformly heated. Such central coke plants have a gas can production of 400 to 500 million cubic meters of gas per year so that any one of these alone could, for instance, furnish the present requirements of our capital, the city of Berlin.

It must be considered as a fortunate coincidence of several independent circumstances that just at a time when the project for long

distance gas distribution became active, the coke industry, for technical and economical reasons, undertook a program of improvement which most favorably influenced the execution of this project. The former conditions would have required a complicated and extensive system of collecting lines. Through the concentration of the coke plants into central plants this network of branches shrinks into one main strand with but a few short feed lines.

Another advantage was gained. It was originally planned that all the coke plants feed the raw gas into the system at low pressure and that at the edge of the Ruhr district central stations for the refinement and compression of gas would be installed. It was hoped that through this centralized refinement of the gas the highest possible economy would be obtained. But in view of the fact that on account of the changes at the coke plants, only very few of them have gas available in large quantities, this idea had to be completely abandoned. The cleaning, compression and metering of the gas are now taken care of at the individual mines. The installation of small uneconomical plants is no longer necessary; rather such large quantities of gas are available at the central coke plants that the maximum of economy in respect to the intended installations has already been reached. Furthermore the equipment and machinery required for the long distance gas distributing system can be supervised by the existing crews at the coke plants whereby a considerable saving in wages and salaries is attained.

For the removal of hydrogen sulphide the dry cleaning process with natural iron hydroxide or other cleaning material has been selected. Although numerous other processes of cleaning have been developed during recent years, including the wet method, and have been tested in actual operation, no other process, either in regard to the cleanliness of the gas, or to safety of operation has proved to be as good as the dry cleaning system. It is quite natural that in a long distance gas supply system of so large a scale only such technical methods can be used where the greatest security is offered in regard to reliability of operation.

Due to the large quantities of gas to be handled daily viz., 300,000 up to 1,600,000 cubic meters in individual plants, cleaning plants are now required of dimensions that had been unknown in Europe heretofore.

The design and construction of the cleaning plants also differs from those heretofore in use. The building covering the cleaning

plant and the covered storage for the cleaning mass such as are customary at most gas plants in Germany, are now completely eliminated. Furthermore we forego the use of a special shed for the preparation of the iron hydroxide. By adding small quantities of oxygen to the gas the material is regenerated in the box proper so that only a single filling and discharging of the boxes is required, resulting in a material immediately salable, containing at least 48 to 50 per cent of sulphur. The charging and discharging of the boxes is done from above. All mechanical equipment, such as extensive and complicated conveyors as far as they are not useful for other operations in the coke plant are eliminated, since they cannot be put to full economical use on account of the intermittent cleaning operation, the filling and emptying of a box taking place only once a year. The cost of cleaning per cubic meter of gas in these installations has been reduced to a fraction of the heretofore usual figure.

The compression of the gas is ordinarily done by means of piston compressors directly coupled to steam engines. This type of machinery was selected on economical and technical grounds. The present possibility of using most of the waste products produced in coal mining for boiler fuel at a high efficiency, either on chain grates or in the shape of pulverized fuel, permits the generation of very cheap steam so that the somewhat unfavorable steam consumption of the piston compressors can be overlooked. In addition to this it must be borne in mind that most of the necessary boiler plants are already in existence and that at most they need only to be enlarged or altered for coal firing. The first cost is considerably reduced and is much lower than it would be if for instance a drive with internal combustion engines had been selected. Furthermore the steam piston compressor is decidedly the safest and simplest in operation, especially in view of the moderate steam pressures and temperatures that are used here.

An electric drive might have been considered if the current were cheap enough, but here another advantage of the piston engine asserts itself, i.e., its flexibility in speed regulation. This can only be approached with an electric drive by the installation of expensive equipment, which unavoidably lowers the efficiency; this is not the case with a steam driven compressor. Furthermore the steam driven piston compressor permits of a higher constant overload.

Turbo compressors due to the low specific weight of the gas are unsuitable for high pressures since these compressors have a rather

low efficiency. They can be used to advantage only where large quantities of gas are to be compressed to a low pressure.

For the intermediate compressor stations where no steam is available other driving machinery such as gas engines, oil engines, electric motors, or, in order to increase the safety of operation, a combination of driving units may be used.

Before the gas enters the long distance system a second cleaning for the removal of naphthalene is provided. The above-mentioned conditions regarding the deposit of naphthalene in the pipe lines and the resulting physical and chemical reactions have developed the fact that the compression to high pressures is the best method for freeing the gas completely of naphthalene and in the simplest manner. For this enterprise a process has been developed which is based on the absorption of the naphthalene from the compressed gases at first at a high and then at gradually lower temperature by a wash oil of special composition. The necessary apparatus for this process is installed directly behind the compressor. A low cost of installation and a minimum of operating expense are the chief advantages of this process.

Following the naphthalene removal intensive cooling of the gas takes place, in order to obtain a gas not only free from naphthalene, but practically free from moisture.

Since the gas is furnished exclusively by coke plants of the most modern design its uniformity and regularity can be relied upon in a degree never before attained. Should a specific heating value or a certain specific weight be demanded, there are no difficulties in the way of meeting such specifications.

Based on the latest investigations and experiments, it is possible to obtain from ordinary coke oven gas a gas mixture of a specific heating value and a specific weight by reaction at high temperature with steam, air or  $\text{CO}_2$ . This so-called coke oven water gas is mixed with the original coke oven gas in such quantities that the mixed gas has the desired heating value and the required specific gravity.

For the metering of gas quantities two measuring systems are used: (1) The direct measuring of volumes (gas holders), (2) velocity measurements.

The most accurate metering can be obtained without a doubt through the ordinary station gas meter where the possibility of error amounts to about  $\pm 2$  per cent. Opposed to its application, however, are the large amount of space required and the high cost of installa-

tion. The gas holder type of meter is supposed to be more advantageous in this regard; there is however no actual operating experience available with this meter.

Compared to displacement meters the velocity meters have the advantage of smaller space requirement and of much lower first cost. Outstanding among these measuring instruments is the Rotari meter (turbine meter), but these meters if employed above a certain size are also expensive to install and in addition to that, the measuring accuracy is poor below 20 per cent of the normal load. For its own purposes, the Ruhrgas Corporation has decided to use the orifice meter at such places, where very large quantities of gas are to be measured as at coke plants located at the mines. The latest investigations gave results which demonstrate that we can figure on an accuracy of  $\pm 2$  per cent with these meters. To guarantee accuracy of metering, parallel meters have been provided so that a switching from one to the other is easily done. In cases where at certain times the flow is considerably below normal, by-passes have been provided into which small station meters have been installed. We thereby obtain in addition to the increased assurance of accuracy, the possibility to investigate at any time the conditions of the orifice meters.

A perfect operation of a long distance gas supply system on such a large scale, with its fluctuations in consumption and the changing of the pressures in the pipe lines is possible only by close and permanent supervision. For this reason we have developed an extensive supervising system which takes care of even the smallest details.

The daily checking of the lines for leaks is done by employees who are stationed along the line where each one has to watch over a certain section. These stations contain at the same time equipment for the measuring of the gas pressure in the line, where the pressure is automatically recorded. In order to have communication by telephone between the individual supervising stations, a combination cable is laid simultaneously with the laying of the pipe line, some of the strands of which are used for telephone service. The other strands serve for the transmission of pressure measurements to a central supervising station. The results of all pressure measurements taken along the lines are gathered in this central station. Furthermore all measurements made at the mines, such as hourly gas quantity, initial pressure, heating value and density of the gas, are transmitted to this central station and automatically recorded. Although

only the recorded readings taken at the mines are used as a basis for accounting, nevertheless perfect control of all the conditions in the whole network is made possible by the collection of all these operating data in one central station.

We believe technical progress has made possible the successful installation of a model long-distance gas supply system.

The idea of long-distance gas distribution is growing rapidly all over Europe and especially in Germany. It will not be very long until the transportation of coal gas over long distances will have found that place in energy economics which it deserves on the basis of technical and economic progress.

# A STUDY OF COMPARATIVE COSTS OF GAS PRODUCTION IN THE RETORT HOUSE

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The object of this paper will perhaps be better understood if, to begin with, I give, for the benefit of those who are not so much interested in carbonization, a short description of the three systems I cover in this paper.

In the continuous working of the vertical retorts, the coal goes in the top and the coke is taken out of the bottom continually, the coal always traveling through the retort.

The ideal method of working them is to insure that the coke going out of the bottom, however you may work the retort for other purposes, contains no more than say one and one-half per cent of volatile matter; the quality of gas made in these retorts can vary, depending on the coal, between 550 B.t.u. down to 400 B.t.u.

In order to get those variations in quality, the throughput of coal is varied and the amount of steam put into the bottom of the retort is varied, and the quantity of fuel used in the producer has to be varied, depending on throughput and the amount of steam put into the bottom of the retort.

It is often stated by all makers of vertical retorts that it does not matter much how much steaming you do, we can always maintain our throughput. That does not go with anyone who has studied the subject of heat transmission.

It is obvious that if you work at your maximum condition, under each of your conditions, then, with materially increased steaming, you must reduce the throughput. With increased throughput, with steaming constant, the fuel consumption per ton remains approximately the same, but per hour increases. The increased steaming will increase the per ton fuel consumption.

It means more fuel per ton, but it perhaps means a little less per therm, and a little more fuel per day. And when you get these factors, all varying, it is very necessary that you know what the bearing is of each alteration on the ultimate results, the only result really that matters,—the cost per therm, whether it is by day or by hour or per ton, or anything else.

You can see, therefore, what the possible variations are in the continuous vertical retorts.

In intermittent vertical retorts, the variations are not so broad. There is a possibility of varying the value with the amount of steaming done. But if heavy steaming is employed, the carbonization has to be increased.

Where no steaming is employed the carbonization may be 10 hours. If there is a low value, say 480 B.t.u., the carbonization time may have to be increased to 15 hours. In that 15 hours, there is the same quantity of coal put into the retort as for the 10 hours. But the water action will increase per ton. It is very doubtful whether the therm per day have been increased at all.

So if coal is high in cost, it may pay you to steam. If coal is low in cost and labor is high and fuel is high, it does not pay to steam.

I never worked out any figures for any gas company that is prepared to take gas at 500 B.t.u. or above, where it ever pays to steam. That is probably a little bit uncommon, but I have worked out many sets of figures, and it has always paid to go to the maximum throughput of coal, subject to getting the number of natural therms per coal, irrespective of steaming.

If you attempt to steam, it is necessary to increase the carbonizing time, the capital cost, and labor, and everything else, but the therms per ton of coal.

In horizontal retorts the main flexibility alteration of condition is in the value of coke used for fuel and in the difference between eight-hour working and twelve-hour working, a reduction in increase of throughput per coal per day per retort per unit of capital per unit of labor, etc.

To save time, I will carry on with the reading of the paper.

#### OBJECT OF THE PAPER

In the following paper an attempt is made to study the comparative importance of the various factors influencing the cost of gas production in the retort house.

#### INTRODUCTION

The cost of gas manufacture is a factor of supreme importance to the gas engineer. A number of factors influence the cost of production, but these factors have not the same measure of importance. At the present day the gas engineer has a number of varying factors.

He has different types of carbonizing plants to choose from; he has different grades of coal which he can treat; under the Gas Regulation Act he can choose the Calorific Value of the gas he is to distribute. In many cases by alteration in throughput of his plant he can increase his thermal output at the expense of therms per ton. Concerning all these variations the question is naturally asked, "What is the effect on the cost of gas per therm?"

The published returns of the gas undertakings furnish little information on this important subject. In order to determine, therefore, the comparative importance of the various factors influencing the cost of gas production in the retort house, the basis of the present study is to make a number of reasonable assumptions and then to vary these assumptions.

The subject is examined from the following aspects.

1. Gas production in continuous vertical retorts:
  - a. Variation in throughput and therms per ton.
  - b. Variation in throughput and calorific value.
  - c. Variation in value of coke.
2. Gas production in intermittent vertical chambers:  
Variation in carbonizing time and calorific value.
3. Gas production in horizontal retorts.
4. Comparison between various systems of carbonizing plant.
5. The relative importance of
  - a. Capital cost.
  - b. Labor.
  - c. Fuel.
  - d. Coal.
  - e. Tar.
  - f. Coke.

The results of the study are contained in a series of tables.

#### 1. GAS PRODUCTION IN CONTINUOUS VERTICAL RETORTS

##### a. *Variation in Throughput and Therms per Ton*

In Table I are given the comparative costs of gas production in continuous vertical retorts making 510 B.t.u. gas, showing the effect of variation in throughput on therms per ton and the percentage of fuel used.

It is known that by variation in throughput a higher thermal yield of gas may be obtained, but this is usually obtained at the expense of a higher fuel consumption in the producers. When treating

a typical gas coal at a throughput equivalent to 0.100 ton per inch retort major axis per day, 78 therms of 510 B.t.u. gas may be expected with a fuel figure of 14 per cent. This set of conditions is shown in Column B, Table I.

TABLE I

COMPARATIVE COSTS OF GAS PRODUCTION. CONTINUOUS VERTICAL RETORTS.  
(510 B.T.U. GAS). VARIATION IN THROUGHPUT AND THERMS PER TON

All figures pence per therm

	SCHEME A	SCHEME B	SCHEME C
Throughput, tons per inch major axis per day..	0.106	0.100	0.094
Therms per ton.....	77	78	79
Fuel, per cent on weight of coal.....	13	14	15
Therms per inch retort major axis per day.....	8.16	7.80	7.43
Coal cost.....	3.430	3.385	3.340
Capital.....	0.293	0.308	0.324
Labor.....	0.110	0.116	0.122
Fuel.....	0.445	0.475	0.500
Total.....	4.278	4.284	4.286
<i>Less</i>			
Gross coke.....	2.451	2.421	2.390
Tar.....	0.713	0.705	0.696
Surplus steam.....	0.257	0.270	0.290
Final net cost per <i>therm</i> .....	0.857	0.888	0.910

*Assumptions*

Coal cost 22/- per ton.

Coke value 22/- per ton.

Capital cost £250 per ton at 8 ton throughput.

Capital charges and maintenance 10 per cent per annum.

Working days per annum 250.

Gross coke yield 71.5 per cent.

Tar yield 11 gallons per ton at 5d. per gallon.

Steam value 20 pence per 1000 pounds

By reducing the throughput a higher thermal yield can be obtained at the expense of a higher fuel consumption. The table is based on a number of assumptions which are set out at the foot of the table. The capital cost item includes foundations, waste heat boilers, coke

and coal handling plant within the retort house, and the building of the necessary retort house, and is based on a plant treating, say, 400 tons per day. The capital charges and maintenance in this table and throughout the rest of the paper, are taken as equivalent to 10 per cent on 250 maximum working days per annum. This figure it is considered is sufficient to pay interest on the money and maintain the plant for an unlimited period at full efficiency. The same basis is taken for all the comparative figures. The value of recovered steam is taken as 20 d. per 1000 pounds, which is considered as a reasonable figure.

Consideration of this table will show that the cheapest gas is made by obtaining high thermal output per inch of retort major axis per day, with consequent low fuel consumption at the expense of high therms per ton of coal. Put in other words, it is cheaper to keep a high throughput with consequent low fuel consumption and lower therms per ton rather than to aim at a higher thermal yield per ton of coal at a lower throughput.

The other factors which are noticeable and which will be discussed at a later stage, are that labor and capital charges are small in comparison with fuel cost.

#### *b. Variation in Throughput and Calorific Value*

Table II shows the effect on cost per therm of working a continuous vertical retort plant at maximum thermal output per day, but reducing calorific value by steaming. Under these circumstances the therms per ton increase from 76 to 90 while the calorific value drops from 500 B.t.u. per cubic foot to 450 B.t.u. per cubic foot, and the throughput falls from 0.106 to 0.085 ton per inch major axis per day.

The fuel consumption based on the weight of coal charged, increases with the fall in calorific value, but due to the fact that the therms per ton increase almost proportionately, there is no variation in the cost of fuel per therm. The interesting fact comes out that so long as the plant is being worked at maximum thermal output, there is little variation in the cost per therm, a negligible alteration in comparison with the final selling price per therm.

It will be noted that the capital and labor charges increase as the calorific value drops. The credit for surplus steam also drops considerably because of the larger amount of steam which is required per therm. Tables III and IV show the steam balance under the conditions of operation as discussed in Tables I and II.

*c. Variation in Value of Coke*

It will be noted that Tables I and II assume that the coal cost and coke value are the same. This, it is suggested, is a very close

TABLE II

COMPARATIVE COSTS OF GAS PRODUCTION. CONTINUOUS VERTICAL RETORTS.  
VARIATION IN THROUGHPUT AND CALORIFIC VALUE

All figures pence per therm

	SCHEME A	SCHEME B	SCHEME C	SCHEME D
Calorific value, B.t.u.....	520	500	480	450
Throughput, tons per inch major axis per day.....	0.106	0.100	0.093	0.085
Therms per ton.....	76	80	84	90
Tar, gallons per ton.....	11	12	13	14
Fuel, per cent on weight of coal.....	13	14	15	16
Therms per inch retort major axis per day.....	8.05	8.00	7.80	7.65
Coal cost.....	3.475	3.300	3.140	2.932
Capital.....	0.297	0.300	0.310	0.314
Labor.....	0.115	0.116	0.119	0.121
Fuel.....	0.451	0.462	0.467	0.469
Total.....	4.338	4.178	4.036	3.836
Less				
Gross coke.....	2.487	2.325	2.182	1.970
Tar.....	0.724	0.750	0.774	0.778
Surplus steam.....	0.270	0.246	0.224	0.186
Final net cost per therm.....	0.857	0.857	0.856	0.902

*Assumptions*

Coal cost 22/- per ton.

Coke value 22/- per ton.

Capital cost £250 per ton at 8 ton throughput.

Capital charges and maintenance taken at 10 per cent per annum.

Working days per annum = 250.

Gross coke yield 71.5 per cent at 520 B.t.u.

Steam value 20d. per 1000 pounds.

approximation to truth, but it may be added that should the value of coke vary relatively to the value of coal, the deductions made from

TABLE III  
STEAM BALANCE. CONTINUOUS VERTICAL RETORTS. (510 B.T.U. GAS)

	SCHEME A	SCHEME B	SCHEME C
Throughput, tons per inch major axis per day..	0.106	0.100	0.094
Therms per ton.....	77	78	79
Fuel, per cent.....	13	14	15
Pounds fuel per therm.....	3.80	4.02	4.26
Gross steam per therm <i>allowing</i> for fan, pounds.	17.1	18.1	19.2
Steam for steaming, pounds per therm.....	3.5	3.4	3.4
Steam for producers, pounds per therm.....	1.1	1.2	1.3
<i>Net</i> surplus steam per therm, pounds.....	12.5	13.5	14.5
Value of surplus steam at 20d. per 1000 pounds <i>pence</i> .....	0.257	0.270	0.290

TABLE IV  
STEAM BALANCE. CONTINUOUS VERTICAL RETORTS. VARIATION IN  
CALORIFIC VALUE

	SCHEME A	SCHEME B	SCHEME C	SCHEME D
Calorific value, B.t.u.....	520	500	480	450
Throughput, tons per inch major axis per day.....	0.106	0.100	0.093	0.085
Therms per ton.....	76	80	84	90
Fuel, per cent.....	13	14	15	16
Pounds fuel per therm.....	3.84	3.93	4.00	4.00
Gross steam per therm <i>allowing</i> for fan.....	17.3	17.7	18.0	18.0
Steam for steaming, pounds per therm.....	2.7	4.2	5.6	7.5
Steam for producers, pounds per therm.....	1.1	1.2	1.2	1.2
<i>Net</i> surplus steam, pounds per therm.	13.5	12.3	11.2	9.3
Value of surplus steam at 20d. per 1000 pounds <i>pence</i> .....	0.270	0.246	0.224	0.186

TABLE V

COMPARATIVE COSTS OF GAS PRODUCTION. CONTINUOUS VERTICAL RETORTS.  
VARIATION IN COST OF COKE

All figures pence per therm

	SCHEME A <sub>0</sub>	SCHEME A	SCHEME A <sub>1</sub>
Coal cost.....	3.430	3.430	3.430
Capital.....	0.293	0.293	0.293
Labor.....	0.110	0.110	0.110
Fuel.....	0.323	0.445	0.567
Total.....	4.156	4.278	4.400
Less			
Gross coke.....	1.782	2.451	3.120
Tar.....	0.713	0.713	0.713
Surplus steam.....	0.257	0.257	0.257
Final net cost per therm.....	1.404	0.857	0.310
Coal per ton.....	22/-	22/-	22/-
Coke per ton.....	16/-	22/-	28/-

Carbonizing conditions as Scheme A, Table I.

TABLE VI

COMPARATIVE COSTS OF GAS PRODUCTION. CONTINUOUS VERTICAL RETORTS.  
VARIATION IN COST OF COKE

All figures pence per therm

	SCHEME C <sub>0</sub>	SCHEME C	SCHEME C <sub>1</sub>
Coal cost.....	3.340	3.340	3.340
Capital.....	0.324	0.324	0.324
Labor.....	0.122	0.122	0.122
Fuel.....	0.326	0.500	0.637
Total.....	4.112	4.286	4.423
Less			
Gross coke.....	1.740	2.390	3.040
Tar.....	0.696	0.696	0.696
Surplus steam.....	0.290	0.290	0.290
Final net cost per therm.....	1.386	0.910	0.397
Coal per ton.....	22/-	22/-	22/-
Coke per ton.....	16/-	22/-	28/-

Carbonizing conditions as Scheme C, Table I.

the first two tables would be fundamentally altered. Tables V and VI are included to elaborate this point.

Table V is based on exactly the same data as given under Scheme A, Table I, but two extra Schemes are put in with this. In all three Schemes, the coal price is kept at 22/- per ton, but in Scheme

TABLE VII  
COMPARATIVE COSTS OF GAS PRODUCTION. INTERMITTENT VERTICAL  
CHAMBERS

All figures pence per therm

	SCHEME A	SCHEME B	SCHEME C
Cycle, hours.....	10	12	15
Calorific value, B.t.u.....	540	510	480
Therms per ton.....	72	78	84
Fuel consumption, per cent.....	14.5	16	17.5
Tar, gallons per ton.....	10	11	13
Coal cost.....	3.668	3.385	3.140
Capital.....	0.310	0.344	0.400
Labor.....	0.105	0.116	0.134
Fuel.....	0.532	0.540	0.550
Total.....	4.615	4.385	4.224
<i>Less</i>			
Gross coke.....	2.622	2.421	2.182
Tar.....	0.684	0.705	0.774
Surplus steam.....	0.200	0.100	0.070
Net cost per therm.....	1.109	1.159	1.198

*Assumptions*

Coal value 22/- per ton.

Coke value 22/- per ton.

Capital cost £280 per ton.

Capital charges and maintenance at 10 per cent per annum.

Working days per annum = 250.

Tar 5d. per gallon.

A<sub>0</sub>, coke is regarded as being worth 16/- per ton, Scheme A, 22/- per ton, and Scheme A<sub>1</sub> 28/- per ton. Similarly, in Table VI, the carbonizing conditions are as in Scheme C, Table I, but here again, although the coal value per ton is kept constant at 22/-, the coke value per ton is varied as follows:

	<i>Per ton</i>
Scheme C <sub>0</sub> .....	16/-
Scheme C.....	22/-
Scheme C <sub>1</sub> .....	28/-

It will be found on study of these two tables that the relationship A/C or A<sub>0</sub>/C<sub>0</sub> or A<sub>1</sub>C<sub>1</sub> are all of the same order, in other words, the comparative A Schemes all give cheaper gas than the comparative C Schemes. These tables also bring out the great importance of coke value per ton. When coke brings a poor value, the importance of fuel consumption is less than when coke brings a good figure.

## 2. GAS PRODUCTION IN INTERMITTENT VERTICAL CHAMBERS

Table VII shows the comparative costs of gas production with intermittent vertical chambers making 540, 510 and 480 B.t.u. gas. It will be seen that Schemes B and C with intermittent vertical chambers correspond with Scheme B, Table I; and Scheme C, Table II, respectively, relating to continuous vertical retorts.

It will be noticed that there is a slight tendency for increased cost per therm when making low calorific value gas in intermittent vertical chambers than when making high calorific value gas. Fuel consumption on intermittent vertical chambers is higher than that of continuous vertical retorts, and in addition to this, the credit for surplus steam is less. Capital cost per therm is slightly higher than that for continuous verticals. These factors result in the net cost of gas per therm usually being higher in intermittent vertical chambers than in continuous vertical retorts.

## 3. GAS PRODUCTION IN HORIZONTAL RETORTS

Table VIII shows the cost of gas production for horizontal retorts. In this case, the thermal yield, fuel percentage, tar yield, etc., are taken from Mr. Hardie's paper to the Institute of Fuel 1926 (*Fuel Economist*, December, 1926). The labor is taken as being the same per ton of coal carbonized as continuous vertical retorts, which leads to a slightly higher labor cost per therm of gas made in horizontal retorts. (See Hardie, Presidential Address, Southern Association Gas Engineers, March, 1927.) The capital cost is taken as £260 per ton, which, including cost of retort house and waste heat boiler, is believed to be a favorable figure for horizontals. The amount of excess steam is also based on the same figures published by Mr. Hardie. It will be seen that the final cost per therm works out

slightly higher than the cost of making gas in Intermittent Vertical Chambers.

TABLE VIII  
COMPARATIVE COSTS OF GAS PRODUCTION. HORIZONTAL RETORTS  
All figures pence per therm

Calorific value, B.t.u.....	540
Therms per ton.....	72
Fuel, per cent.....	15
Coal cost.....	3.668
Capital.....	0.347
Labor.....	0.126
Fuel.....	0.550
Total.....	4.691
Less	
Gross coke.....	2.622
Tar.....	0.660
Surplus steam.....	0.222
Final net cost per therm.....	1.187

*Assumptions*

Coal cost 22/- per ton.  
Coke value 22/- per ton.  
Capital cost £260 per ton.  
Capital charges and maintenance at 10 per cent per annum.  
Gross coke yield 71.5 per cent.  
Tar yield 9.5 gallons per ton.  
Steam value 20 pence per 1000 pounds.

#### 4. COMPARISON BETWEEN VARIOUS SYSTEMS OF CARBONIZING PLANT

Table IX shows the comparative costs of gas production in various types of carbonizing plant.

Continuous vertical retorts are shown making 510 B.t.u. gas and 480 B.t.u. gas; intermittent vertical chambers making 540, 510 and 480 B.t.u. gas; horizontal retorts are shown making 540 B.t.u. gas. In considering this table it is to be remembered that in each case the following items are the same.

1. Coal cost 22/- per ton.
2. Coke value 22/- per ton.
3. Tar value 5d. per gallon.

TABLE IX  
COMPARATIVE COSTS OF GAS PRODUCTION. VARIOUS CARBONIZING SYSTEMS  
All figures pence per therm

	CONTINUOUS VERTICAL RETORTS		INTERMITTENT VERTICAL CHAMBERS			HORIZONTAL RETORTS
	510	480	540	510	480	
Calorific value B.t.u. per cubic foot.....						540
Therms per ton.....	78	84	72	78	84	72
Fuel consumption, per cent.....	14	15	14.5	16.0	17 5	15
Tar, gallons per ton.....	11	13	10	11	13	9.5
Coal cost.....	22/-	22/-	22/-	22/-	22/-	22/-
Coke value.....	22/-	22/-	22/-	22/-	22/-	22/-
Coal cost.....	3.385	3.140	3.668	3.385	3.140	3.668
Capital charges.....	0.308	0.310	0.310	0.344	0.400	0.347
Labor.....	0.116	0.119	0.105	0.116	0.134	0.126
Fuel.....	0.475	0.467	0.532	0.540	0.550	0.550
Total.....	4.284	4.036	4.615	4.385	4.224	4.691
Less						
Gross coke.....	2.421	2.182	2.622	2.421	2.182	2.622
Tar.....	0.705	0.774	0.684	0.705	0.774	0.660
Surplus steam.....	0.270	0.224	0.200	0.100	0.070	0.222
Net cost of gas per therm.....	0.888	0.856	1.109	1.159	1.198	1.187
Data from.....	Table I Scheme B	Table II Scheme C	Table VII Scheme A	Table VII Scheme B	Table VII Scheme C	Table VIII

4. Capital charges and maintenance = 10 per cent per annum.
5. Working days 250 per annum.
6. Value of surplus steam 20d. per 1000 pounds.

Examination of this table brings out the following facts:

- a. The cheapest gas is made in continuous vertical retorts, followed by intermittent vertical chambers, and then by horizontal retorts.
  - b. The variation between the highest and the lowest cost of production is not more than one farthing per therm.
  - c. Intermittent vertical chambers have a higher fuel consumption than continuous vertical retorts when making the same calorific value gas.
  - d. Continuous vertical retorts give a greater yield of surplus steam than intermittent vertical chambers when making the same calorific value gas.
5. THE RELATIVE IMPORTANCE OF THE VARIOUS FACTORS GOVERNING THE COST OF GAS PRODUCTION

Table IX gives an opportunity of studying the relative importance of the various factors governing the cost of gas production.

*a. Capital Cost*

Consideration of this item shows that the highest capital cost is found with intermittent vertical chambers making 480 B.t.u. gas, with a charge of 0.400 pence per therm, and the lowest with continuous vertical retorts making 510 B.t.u. gas with a charge of 0.308 pence per therm; when making 540 B.t.u. gas, horizontal retorts show a slightly greater capital charge than intermittent vertical chambers, the figures being 0.347 and 0.310 pence per therm respectively. The small difference in ultimate capital cost per therm shows the importance of choosing a plant suitable for the particular circumstance under which it is to operate rather than on the basis of cheapness. To give an example: On an installation to make 6 million cubic feet per day, an extra £20,000 in original capital cost affects the cost of gas only to the extent of 0.06 pence per therm.

*b. Labor Cost*

The weekly wage bill is one of those tangible expenses which it is possible to economize on, but it is to be remembered that the labor cost per therm is a very small item in the retort house. Labor cost

varies from 0.134 to 0.105 pence per therm in the figures considered (Table IX). To sacrifice efficiency for the purpose of saving a few pounds in wages is poor policy.

### *c. Fuel Cost*

Fuel cost is one of the most important items in the cost of gas production. Consideration of Table IX will show that fuel cost is approximately 3 times as important as labor, therefore every effort should be made to keep fuel consumption low. There are three means by which the fuel account may be kept down,

- a.* By having producers of ample capacity.
- b.* By staffing the producers with sufficient labor to ensure regular attention.
- c.* By having the installation suitably insulated to prevent loss of heat by radiation.

In connection with fuel cost it must be remembered that modern carbonizing plants are provided with waste heat boilers which give a valuable credit to the process. It is the *net* fuel cost (i.e., fuel to producers less value of surplus steam produced) which is of importance in determining final cost of gas per therm. The net fuel costs under the various schemes as set out in Table IX are given below:

#### *Net Fuel Cost per Therm of Gas*

	<i>Pence per therm</i>
Continuous vertical retorts at 510 B.t.u. gas.....	0.205
Continuous vertical retorts at 480 B.t.u. gas.....	0.243
Intermittent vertical chambers at 540 B.t.u. gas.....	0.332
Intermittent vertical chambers at 510 B.t.u. gas.....	0.440
Intermittent vertical chambers at 480 B.t.u. gas.....	0.480
Horizontal retorts at 540 B.t.u. gas.....	0.328

To obtain a picture of the relative importance of the three factors, capital, labor and fuel, on the conditions as set out in Table IX, the following statement may be of use.

It will be found that:

- a.* Sixteen per cent extra capital expenditure on the original plant,
- b.* Forty per cent extra labor in running the plant,
- c.* Ten per cent extra fuel (i.e., increase in fuel figure from 14 to 15.5 per cent on weight of coal),

all have an equal effect on the final cost of gas manufacture per therm.

*d. Coal*

In all methods of carbonization the cost of coal is by far the most important item. By suitable regard to the coke market it is, however, usually possible to obtain a credit of from 50 to 70 per cent of the coal value in the form of coke. It is outside the scope of the present study to discuss in detail coal cost, as in all the tables coal price has been kept constant. The effect of the relationship between coal and coke value has been discussed in Tables V and VI. Generally speaking it pays to use the cheapest available coal which (a) can be carbonized satisfactorily in the plant, (b) produces a satisfactory coke with a reasonable ash content.

*e. Tar*

The importance of tar is shown on Table IX. It may not be generally realized that the credit for tar is sufficient to pay for capital charges, labor, and a portion of the fuel cost. This shows the necessity of ensuring that the maximum return is obtained from the tar by careful marketing in crude form, or alternatively, by its conversion into dehydrated tar or distillation products.

*f. Coke*

The figures shown in the various tables emphasize the great importance of coke. It will be noted that throughout the fuel cost has been debited as a working expense and the full credit given for the entire production of coke. It will be seen with particular reference to Tables III and IV that any steps which increase the quantity and market value of coke are likely to be very well justified.

The production of good coke reasonably free from ash and moisture and screened into several suitable sizes, with a good sales organization, is a most important factor in the production of cheap gas.

## CONCLUSION

The most significant point which this study brings out is that the carbonizing conditions may be varied over wide limits without making any large difference in the final cost per therm. It is probably a statement of fact that at the present time, the average selling price of gas in London, including the industrial load, is over three times the cost actually involved in the preparation of the crude gas. If this is the case there is surely a lack of true perspective in straining

unnecessarily to cut the capital cost of a new installation, when one which is to cost £20 per ton capacity more, may be more efficient to run and give a better layout for the particular circumstances. The same thing applies to the tendency to operate a plant with the absolute minimum of labor, often at the cost of the efficiency of the plant.

The gas industry has rather accepted the point of view that "profits are made in the retort house." At the present time this proposition seems to demand a corollary that "profits are lost outside the retort house." The problems of economic distribution, scientific main laying and improved methods of the sale of gas and coke would appear to be lines in which there are far greater opportunities of saving money than there are in the modern retort house.

# THE GAS AND TAR INDUSTRIES IN FRANCE

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## I. THE GAS INDUSTRY IN FRANCE

Important changes have occurred in the gas industry of France since 1914. In order fully to understand these developments, it is well to review briefly the situation prior to the war.

Distribution of gas was recognized as a public utility, and subject to public regulation. This regulation, however, was not uniform. Generally, the conditions imposed had to do with fixing the price at a flat rate; defining the quality of the gas in terms of minimum illuminating power, its contents of carbon monoxide, sulphuretted hydrogen, and sulphur; stipulating the quantity to be delivered to public and to private consumers; and setting the pressure of delivery. Interruption of distribution was permissible in very few circumstances, (strikes, etc.).

Gas had lost much of its importance for lighting purposes, and was used mainly for heating. Some tendency toward the consolidation of small companies into large gas distributing units was to be observed. Gas was available in nearly all cities of 15,000 and over, and in smaller communities near sources of supply. The coal used in production of gas was obtained in about equal quantities from French, English and German fields. Buying of gas in large quantities from coke ovens by distributing companies was unknown.

Horizontal retorts were mostly used, though some of the largest new companies showed a preference for inclined retorts, or for large chambers either vertical or inclined, which offered certain economies. Continuous processes of carbonization were not used.

The war forced the government to adopt a policy of coal conservation which resulted in special regulation of the gas industry; illuminating power was disregarded as a standard specification and benzole removal was made compulsory in several works.

Since 1921 new contracts for gas distribution must comply with standard rules summarized as follows: gas may not be required to possess a calorific value of more than 4500 calories per cubic meter (about 500 B.t.u.). Its content of carbon monoxide may not exceed

fifteen per cent; it must possess a characteristic odor. A sliding scale is foreseen for flat price rate per cubic meter and refers to coal, by products and wages indexes.

Since 1923 removal of benzole has been or will be made compulsory for plants producing 1,800,000 cubic meters or more a year.

During the period of reconstruction of the devastated districts amalgamation of works occurred and led to distance distributions like at St. Quentin, Noyon (25 miles).

Coking plants have become an important source of gas supply in certain districts where coke oven operators have a surplus of gas which they cannot use for chemical industries (synthetic ammonia, methanol, ethanol, etc.). Distributing concerns buy it in bulk, but must make provision for continuance of their service in case of interruption of the coking business, as it would not be a legal excuse for interruption of distribution. The situation has improved somewhat since compound coke ovens have appeared. Examples of development are to be found in the eighty mile distribution system, Bethune to Villers Bretonneux; in the twenty-five mile system, Lens Douges Courrieres to Lille Roubaix Tourcoing; in the twenty mile distribution system, Moyonore-Metz. Local distributions have to be quoted at Donai, Thionille, Montlucon and St. Etienne (for part of the consumption).

There exist in France, as in the United States, coke oven plants, having gas distribution as their main object: examples are Toulouse, Gennevilliers, (cokeries de la Seine) and Strasbourg. In this last example gas is distributed to thirty miles, reaching Selestat.

*Present State of Gas Industry in France.* Following are statistical data on the present gas industry in France:

4 works with an annual output of more than 100,000,000 cubic meters (3,500,000,000 cubic feet).

15 works with an annual output between 10,000,000 and 100,000,000 cubic meters (350,000,000 and 3,500,000 cubic feet).

152 works with an annual output between 1,000,000 and 10,000,000 cubic meters (35,000,000 and 350,000,000 cubic feet).

431 works with an annual output less than 1,000,000 cubic meters (35,000,000 cubic feet).

Total consumption of coal is 5,000,000 tons a year; sales of gas coke reach 2,500,000 tons.

Number of people employed is about 55,000.

Total capital investment is over 5,000,000,000 francs (\$200,000,000); actual value, according to last quotations is about \$1,000,000,000.

We shall examine, briefly, some characteristic features of the gas works classified, in four categories: extra large, large, middle, and small.

Extra large works are: The Paris Gas Company, the Paris Suburban Area Company, (this being properly named Light, Heat and Power Company, i.e., "Société d' Eclairage, Chauffage & Force Motrice," or by abbreviation, "E. C. F. M."), and the Lyons Gas Company and Marseilles Gas Company.

The city of Paris has a limited area and gas consumption may increase only by increasing the individual use of gas. As there are not many industries in Paris, domestic consumption is by far the most important and will always be. Public lighting, however, is done by compressed gas in many districts, and elsewhere gas lamps are still maintained for emergency purposes. Years ago, Paris was divided into many districts, each possessing its own small gas works. Through successive amalgamations, distribution has been concentrated in one organization. The city eventually took over the works and mains; and the whole system is now operated under contract by the Paris Gas Company. It has been possible to reduce the number of works and to concentrate output in several works. A plan has been adopted to combine all the old plants into three companies. At present gas is made in these extra large works (two outside, and one inside the city of Paris) and four smaller ones all located in the city.

The Paris suburban area is not so strictly limited as Paris the city. Extension of distribution to new localities and to many industries is possible. The distribution system is an amalgamation of smaller units. The "E. C. F. M." has concentrated its production in one plant.

Paris Gas Works (extra large). *a.* The "Landy" plant is the largest. It is at Saint-Denis, three miles North of Paris. It has horizontal benches with a total daily output of 720,000 cubic meters (about 25 million cubic feet), and a water gas plant, somewhat more modern, of 270,000 cubic meters (10 million cubic feet) daily capacity. The "Landy" plant has been somewhat modernized by substitution of silica for the ordinary refractory material. Mechanical handling and transportation are up to date and generally used.

*b.* A more modern plant is located at "Clichy," two miles West of Paris. Equipment consists actually of four batteries of eight ovens of two Woodall Duckham retorts. Each retort has a distilla-

tion capacity of  $6\frac{1}{2}$  tons a day. By steaming practice, a ton of coal furnishes up to 420 cubic meters (15,000 cubic feet) of a gas possessing 4,500 calories to the cubic meter (500 B.t.u. per cubic foot). The capacity of the "Clichy" works will be soon trebled and the old gas works in the city will be closed. When the "Clichy" plant is completed 72 cubic meters of gas will be made a day per square meter of total area of the works (2,800 cubic feet per square yard); and the output per workman will reach 4,500 cubic meters a day (16,000 cubic feet). Retorts are heated by producer gas; independant producers of the Kerpely Maischaka type with automatic scale removing devices have been adopted. They have the appearance of a water-jacketed oven.

c. The third plant is in Paris itself (La Villette). It contains inclined chambers of the Munich's type. Daily output is 450,000 cubic meters or 16 million cubic feet. Research laboratories are contiguous to the plant.

The "E. C. F. M." has a single plant at Gennevilliers. The circumference of the area served is about 160 miles; length of mains is 1,800 miles or enough to extend from Washington, D. C. to Denver, Colorado. The total output of coal gas from either horizontal retorts or inclined chambers amounts to 700,000 cubic meters a day (nearly 24 million of cubic feet). Since 1925 an entirely automatic water gas plant (Humphreys and Glasgow) has been in operation; the daily capacity is 268,000 cubic meters of blue gas or 328,000 of carburetted water gas (that is  $9\frac{1}{2}$  million or  $11\frac{1}{2}$  million cubic feet). Only twelve workmen (working in three shifts of three men each, with three extra men) are necessary. Another feature is a telescopic gas-holder of 225,000 cubic meters (or 8 million cubic feet).

The Lyons Gas Company has a distribution area comprising part of Lyons City and many suburban districts. Gas is produced in several plants. The "La Mouche" plant has the largest dry gas-holder in France. Horizontal retorts are used, heated by producer gas made in a central station.

Marseilles has adopted an electrostatic plant for precipitation of tars.

*Large and Medium Works.* Increased wages led gas companies which had to rebuild or extend their works to adopt continuous distillation processes, even in middle class works, notwithstanding the very high first costs.

Woodall Duckham retorts have been erected at Montbéliard,

Rennes, and Colmar with capacities of 25,000 cubic meters or 900,000 cubic feet a day, while Glover West retorts have been adopted at Villemomble, Blois, with capacities of 15,000 cubic meters (550,000 cubic feet a day). Steaming is generally done. The average production of gas per ton of coal is about 450 cubic meters, or 16,000 cubic feet.

Discontinuous vertical chambers are numerous. They are made as a rule of silica; average production is 400 cubic meters (14,000 cubic feet) per ton of coal. Steaming is generally not done. Coke consumption for distillation varies from 14 to 17 per cent of the production.

Water gas plants have been erected since 1920. We must also say a few words about integral gasification. Two kinds of plants, both of foreign origin, may be found. Tully plants (14,000 cubic meters, 500,000 cubic feet a day) are used at Lille, Biarritz, Versailles. Nanterre, Cannes, and St. Raphaël use the Kreisa type. Strache plants may be adopted by other cities.

The removal of benzole being, in general, compulsory, oil washing has been widely adopted. Several plants use a continuous process developed by Mr. Guillet (Manager of Besançon Gas Works); its main feature is utilization of waste heat; this system is used at Besançon, Dijon, and Avignon. Oil used is tar oil and not straw oil.

Chervet's process also uses tar oil. Extraction of benzole is made either at atmospheric pressure or under vacuum. The main feature is that washing oil is circulated without any contact with air. Vacuum allows a great reduction in steam consumption (three parts of steam for one part of benzole in weight); absence of contact with air means a saving of one-fourth to one-third in oil consumption. This process is operated at Lyons ("La Mouche").

The tetralin process of benzole recovery is used at Melun. Activated charcoal has been adopted at Versailles, Nanterre, Fontainebleau, and elsewhere. The steam consumption amounts to four parts of steam for one part of benzole.

*Small Works.* Many small works have disappeared by amalgamation. Works still existing generally have horizontal retorts. At Chateaudun, however, vertical chambers have been adopted for a daily output of 2,400 cubic meters, or 85,000 cubic feet.

In all works, in the smallest as well as in the extra large ones, mechanical handling and transportation have been, or will be adopted; another characteristic feature is the improvement of coke quality by

careful screening and sizing and reduction of moisture to a normal degree.

Gas pipes are either of steel or of cast iron. For long distance transmission, both types have been used.

Companies often possess gas works in different localities, and frequently distribute electricity in the same cities.

*Research Laboratories.* The Paris Gas Company has at La Villette:

a. An experimental plant.

b. A research laboratory for physics, conducted by Professor Chappuis. Researches relating to effect of parasite electric currents on mains, and inflammability of gas-air mixtures have been conducted there.

c. A research laboratory for chemistry, conducted by Professor Mailhe. A paper presented by him at this conference gives an example of his work; we may also say that researches on benzole purification, synthetic motor fuels, etc., are made.

In addition, a laboratory for testing gas appliances is maintained at Paris.

The "E. C. F. M." Company has control and research laboratories at Gennevilliers. Chemical researches by Mr. Leroux on fabrication of pure phenole, pure naphtalene and pure benzene have been made there. Studies in gas-oil cracking for carburation of water gas and in benzole removal are also conducted.

The Bourbonnais Gas Company has laboratories at Lyons where research in gas appliances are conducted. Marseilles Gas, Lyons Gas Company and many others also have research or control laboratories or both. The alliance between science and practice is well established in the French gas industry.

*Market and Distribution.* Although electricity has replaced gas for lighting purposes to a great extent, gas will always have a large field of usefulness in public lighting. Paris, for instance, maintains gas lighting, for part of the city and in parts where electric lighting takes place, gas emergency service is provided.

Another new field for the use of gas is appearing in the automobile. Coal gas may be used in ordinary motor cars. For many years gas has been used by the most important French car builders for running their motors in bench tests. Use of gas on the road is possible. The difficulty is to stock gas. The risk of explosion due to the presence of oxygen in gas and the possible reaction either with hydrogen or methan at certain pressures has been studied by Professor

Chappuis at the Paris Gas Company, who proved that there was no danger even at pressures of 100 and 200 atmospheres (1,400 and 2,000 pounds per square inch), if oxygen contents of gas were less than 8 per cent. As the oxygen content is actually less than 4 per cent, use of compressed gas is possible.

Another objection to the use of gas for automobiles has been eliminated by the recent invention of lighter containers for the gas. Motorbuses using compressed gas took part in the National Rally in July, 1928. The containers were refilled at the coke ovens or at the gas works by compressors. A transport contractor of Paris recently ordered twelve motor trucks designed for gas use.

The principal field, however, for gas distribution is heating.

Domestic uses for cooking ranges, irons, stoves, refrigerators, gas fires, central heating boilers, for example, are too well known to require enumeration.

In regard to industrial heating, I shall merely quote the American Gas Association slogan to show what a broad field of development has to be foreseen. "If it is done with heat you can do it better with gas."

It is necessary to say a few words also about gas industry by-products: coke, benzole, ammonia and tar. Tar is dealt with further on; benzole, besides chemical (dyestuff and synthetic drugs industry) and solvent (rubber industry) uses, has a broad market as motor fuel, either pure or mixed with gasoline. Its principal features are higher thermal capacity for a given volume, higher useful compression ratio, hence better thermal efficiency. The airship "Bremen" gained 25 per cent of flying radius by using benzole; and as the plane landed at Green Island with tanks nearly empty, one may surmise what would have happened in case of another fuel having been used. Ammonia is used either for chemical purposes (Solvay's process for instance) or as a fertilizer. Gas coke, by far the most important by-product, is an excellent smokeless fuel either for domestic purposes or central heating, or for certain industries. Gas coke must be as dry as possible and sized carefully for sales. The price of gas coke a few years ago was lower than that of metallurgical coal; in France as well as in England, the situation is now reversed. Gas coke is very suitable for the calcium carbide industry and water gas producers, and part of a plant's output is used on the spot for this use.

*Prospects of French Gas Industry.* The gas industry will grow. The gas industry and the coke industry will be more and more closely

connected; and gas distributing companies will buy gas in bulk from coke ovens, everywhere that there is assurance of a sufficient quantity available.

It is certain that amalgamations will continue, with resultant saving of labor and improving of efficiency. Gas works will adopt, more and more, discontinuous processes such as horizontal chambers similar to actual coke ovens, or vertical retorts, or continuous vertical retorts. Silica will be substituted for ordinary refractory material. Mechanical methods of handling and transportation will be improved. Water gas plants will be erected in increasing numbers and will act as flywheels in certain cases.

Extension of gas distribution to adjoining localities will occur, and initial distribution pressure will be increased, to assure a sufficient pressure at the place of consumption.

It may even be forecast that, as with electricity distribution, inter-connections between different works will appear, as they have in America.

Coöperation with low temperature carbonization is possible. Continuous distillation in vertical retorts may be considered as a transition stage between the high temperature carbonization, as practiced in coke ovens, and certain processes of low temperature distillation. We need, however, more practical knowledge of low temperature carbonization practice before adopting definite conclusions.

To sum up, the gas industry has a promising future, and a field is open for research work in production, distribution and utilization. The purpose of this research will be the saving of labor and of coal, the recovery of waste heat and the improving of efficiency in utilization.

## II. THE TAR INDUSTRY IN FRANCE

Coal tar is produced either by the gas-works or by the coke ovens plants. In 1913 by-products ovens had an annual output of three millions of tons of coke; in 1920 most of our plants were destroyed and need of tar and its derivatives was so urgent that exportation had to be prohibited.

Since that time construction of coke ovens has taken a great development and the following figures show the corresponding rate of the increase of tar production in the past four years.

YEAR	TAR FROM GAS PLANTS	TAR FROM COKE OVENS	TOTAL
1924	230,000	174,000	404,000
1925	236,000	200,000	436,000
1926	238,000	227,000	465,000
1927	237,000	254,000	491,000

Until 1913, tar was distilled chiefly by independent distillers. Changed conditions have brought about a closer alliance between the distilleries and the sources of production, as well as a trend toward the consolidation of small distilleries into large units. Most distilleries now belong to producers, or groups of producers, or are operated on a coöperative plan between the producers and distillers.

Tar was always distilled by a discontinuous process in France until 1918. The usual capacity of the stills in the larger and more modern plants was about 20 tons. Stills of this capacity were found to be the most efficient, and became the most prevalent type. Mixing device (Mallet's agitators) were generally used. Distillation under vacuum and distillation under pressure were tried without satisfactory results. In both cases, difficulty was experienced in keeping the stills and the joints sufficiently air-tight.

Dehydration of the tar also offered difficulties. Tar contains water in two conditions: Water that is mechanically mixed with it, and water that is almost a constituent of the tar. The latter, amounting to 8 or 10 per cent and sometimes more, could not be removed by a process of settling. Mechanical devices, employing the centrifugal principle, were tried without success. Previous distillation was found to be the only adequate method of dehydration. It was possible by this method—of which there were several processes—to reduce the time of distillation (including dehydration) from 24 to 16 hours.

Because of the various disadvantages of the discontinuous process, however, attention was given to development of a continuous process. A number of methods have been tried. After the war two Raschig (Garman) plants were erected in France, but this method has not since been extended. A process developed by the Messrs Burt, Boulton and Haywood has also been tried. This method employed seven or eight stills working in series. Tar was pumped from one still to another and heated progressively from still to still. The method could be used only by large plants having at least seven stills.

Sulzer devices were also tried in France. The most modern process of continuous distillation thus far used in my country, however, is the "Ab-der-Halden."

The theory and details about the "Ab-der-Halden" process are given to you in another paper, so I will mention but a few of its notable points. Units have from 1 to 50 tons daily capacity. First costs are not as high as in other continuous processes. Labor requirements are slight. The coal and gas consumption for heating is very small. The consumption of steam is somewhat high, but generally steam may be easily obtained at very low price by recovery of waste heat, and an especially notable feature is the exceedingly small dimension of the plant.

*Treatment of Phenolic Oil.* Saturation of phenates is obtained now by carbonic acid more often than by sulphuric. The treatment of phenols varies according to the manufacturers but includes generally many distillations and rectifications. It is possible by a very close rectification to obtain phenol, orthocresol and a mixture of three cresols. Separation of the three cresols requires two sulphonations. That treatment is made but in two or three stages chiefly in view of getting cresols, as phenol is obtained in larger quantities by the synthetic process than by the distillation of crude phenols coming from tar.

*Treatment of Naphthalene.* The complete treatment includes acid washing, distillation, rectification, but it is very important to start from a sufficiently pure crude product.

Naphthalene obtained by settlement of naphthalenic oils always contains an important percentage of oils. Treatment by pressure only, even at a temperature of about 120°F. is not fully satisfactory. It has been found that a centrifugation of crude naphthalene, with addition of water at about 140°, improved the quality of pressed naphthalene. Another method is to wash crude naphthalene with benzole. It is then possible to obtain a crude naphthalene containing only traces of oils. Pressing is not longer necessary. The recovery of benzole is satisfactory, as losses are very small. The regulation of the temperature of distillation and of the rectification column requires care.

Having reviewed the technical side of the tar industry in France, let us now turn our attention to the economic side.

Tar may be used in crude or refined form, or it may be subjected to distillation.

Crude tar may be used as a fuel in metallurgical ovens.

The refined tar has its principal use on the roads.

Tar submitted to distillation furnishes light oils, phenols, naphthalene, anthracene, pyridine, creosote oil, washing oils, fuel oils, Diesel oil, and pitch.

If we take into account the cost of refining, or of distillation, with additional charges relative to those treatments, (investment, amortization, distribution service, etc.), we find for tar three values: one as fuel, one as road material, and one as source of chemical compounds. The tar producer is interested in disposing of his tar in such a way as to receive the most money. It is not advisable, generally speaking, to burn tar. It has its minimum market value as fuel. The useful products are lost; and it is generally impossible to treat other fuels so as to obtain chemical compounds or to use them as road materials. But if tar production continues to increase, it may happen that the production of derivatives will exceed the market demand and even that an excess of tar as road material will exist. In this case, tar as liquid fuel will always have a certain value. This will act as a safeguard for the producer.

The value of tar as a road binder is bound to the value of the competitive substance, bitumen. Bitumen is spread more easily and generally dries quicker than tar. (When I speak of tar used as road material, I consider prepared or refined tar and not crude tars, which generally do not pass road specifications.) On the other hand, tar sticks to the substratum better than bitumen, and for the first coat tar is preferred. In wet weather a car stops more quickly on a road covered with tar than on a road covered with bitumen. Experiments made by Professor Brix of Charlottenburg, Berlin are quite conclusive. This advantage of tar is more pronounced at high speed. Cars do not skid on tar roads as much as they do on bitumen or asphalt roads. Mixtures of tar and bitumen have been tried and may be, in certain cases, a good solution. Anyhow, the value of tar as road material must be approximately equal to the value of bitumen. A very large field is open to both products.

We must next consider the products of distillation. Light oils have a very broad market; but benzoles, toluol and solvent-naphtha removed from gases evolved during high temperature carbonization, are more abundant than light oils extracted from tar by distillation. In addition, the percentage (about 1 per cent) of light oils in tar is very small, and they have no effect on the price of tar.

Crude phenols are chiefly a source of cresoles; and synthetic phenol is available on the market whenever phenol is produced in large quantities. Naphthalene may be extracted from middle oils by settling, and then refined; or it may be left in those oils when they are used as timber preservatives. The naphthalene market consists chiefly of dyestuff manufactures. It will always be found in sufficient quantities for peace-time needs. In war-time, however, naphthalene has great value as source of high explosives.

Anthracene and pyridine have a very small market; anthracene was formerly raw material for the manufacture of alizarin, but now a synthetic process of alizarin fabrication employs naphthalene as crude material. Pyridine was used chiefly as a denaturing agent for ethanol but has been superseded by methylic spirit, and is practically without a market.

If we except naphthalene to a certain extent, we see that the value of distilled tars depends on two chief factors, oils and pitch. Oils are used:

1. For benzole extraction, (competing in Europe with straw oil, activated charcoal, etc.), and for gas purification. Such classes of oils have the greatest value.

2. For wood preservation, where they have the next greatest value as far as price is concerned.

3. For Diesel engines and metallurgical ovens, in competition with gas or fuel oils.

Pitch still remains and there is a certain relationship between quantities of pitch and of oils. The proportion may be changed, and the ratio of pitch to oils slightly reduced in certain processes where oxydation during distillation is avoided. That is the case in the "Ab-der-Halden" process, for instance. However, for one part of oil, we have always between 2 and  $2\frac{1}{4}$  parts of pitch. The disposal of pitch is then the main problem of tar distillation.

The manufacture of varnishes and roofing material will never create a sufficient demand to all the production possibilities which would amount to 65 per cent of the tar produced, if all the tar should be distilled.

Extra dry pitch may be pulverized and used as a solid fuel, but its value is then less than the value of tar for the same purpose, since liquid fuel always has higher market value than a solid one.

Pitch may be used as a raw material for electrode coke manufacture. The demands for such material are, however, limited. The

most important market of pitch has been in briquette manufacture, but briquette production is decreasing because of the electrification of railways and substitution of fuel oil for briquettes in the steamships, etc. The advent of boilers with under-feed stokers in which it is possible to burn slime or slacks without previous agglomeration, and of new uses for pulverized coal has also decreased the briquette market.

Hence, French tar producers and distillers have to face the problem of selling an increasing part of their tar for road material or of finding new uses for pitch, as the tar oil market is always sufficient.

Researches on this subject are in progress. Chemists are trying to hydrogenate tar. Professor Hugel, of the National School of Petroleum, in Strasbourg, has obtained lubricating oils by means of alkaline metals or their hydrides. Experiments will be continued.

Messrs. Kling and Florentin at the Municipal Laboratory of Paris have succeeded in obtaining marketable liquid products by another process.

We believe that our German colleagues must also face this problem, and will make some experiments at Meiderich.

French chemists have found that pitch is the binding material of tar, and that, for road purposes, only binding material is necessary. Experiments have been made in the use of pitch on the road.

It was first tested by spreading soft pitch at high temperature ( $180^{\circ}\text{C}.$ ), but, when cooled, the pitch became too brittle and the carpet did not last. Mixtures of pitch and bitumen were tried but were not found satisfactory. By mixing pitch with several products, however, Professor Baume has obtained a solid chemical compound, which may be used as a dispersion agent for hot water, and the emulsion of water in pitch is an excellent road material, either as a carpet on any kind of base, or as a binder for macadam or in grouting processes. As the market for road materials is practically unlimited, tar distillers have now a better future. They may distill tar, keep the oil, and have two main markets for pitch. Prospective successes of chemical researches in hydrogenation will improve the situation.

The tar industry in France is robust and active, coöperation between this branch of industry and technical science is especially important because of changing economic conditions which necessitate frequently finding new uses for tar derivatives. Conditions in the United States are quite different, it is true, from conditions in France, but I hope that the description of the situation in my country may have interested American tar producers and distillers.

## DISCUSSION

J. B. GARNER (Hope Natural Gas Company, Pittsburgh, Pa.): I would be interested in knowing from Dr. Roelen the approximate average content of oxygen and of carbon monoxide in the gas which is transported under the pressures mentioned, and in a statement, if possible, of his experience with the corrosive effect of these constituents on the material of the pipe lines, and the material in compressors.

DR. ROELEN: The content of oxygen is about one-half of a per cent in the final gas, and the content of carbon monoxide is about 6.5 per cent.

The practice to add some oxygen to the gas has been in use in Europe for several years and also in coke plants, which, since 1919 have furnished gas to the cities by distribution, and in this time there have been reports of corrosion either in the compressor or in the lines.

We also have found no evidence of corrosion by oil gas. We also deliver in some cases, oil gas from the coke plants to the steam lines over distances of ten miles, and we make no statements of corrosion there.

MR. GARNER: I am interested also in the sulphur content, and in the possibility of the combination of the carbon monoxide of the gas, under high pressure and at a certain temperature, with the iron of the steel to form iron carbonyl, which later on might result in deposits in the lines, etc.

Is the oxygen which is in the gas, at the present time, of sufficient partial pressure to unite with the iron of the steel and form a dust with the subsequent result of the stoppage of meters at points of distribution?

DR. ROELEN: There have been no obnoxious effects from the oxygen nor on the addition of oxygen to the gas. I can give you some data later on this. I think Professor Bunte could give you some data on this. He made the studies.

E. L. COFFMAN (Public Service Electric & Gas Company, Camden, New Jersey): I would like to inquire as to the B.t.u. value of the gas before compression and B.t.u. loss due to compression.

DR. ROELEN: We make no statement that there is a difference, only after the compression and taking out the naphthalene by this new process. Then by the same process the moisture is taken out.

The B.t.u. is increased naturally on account of the gases having no moisture. The gases in general have a heating value of 4500 calories per cubic meter. I do not know what it is per cubic foot.

F. ZUR NEDDEN (Secretary, Fuel Committee of Reichskohlenrat, Berlin): About 550 B.t.u. per cubic foot.

DR. ROELEN: And after the moisture is taken out the calories increase up to 4700.

CHAIRMAN FULWEILER: That does not sound right. The translation of figures does not seem to be correct.

DR. ROELEN: 4500.

CHAIRMAN FULWEILER: Was the increase afterwards?

Put it on record: The increase in heating value after compression, due to the loss in water vapor and other things, is about 1 per cent.

R. W. MILLER (Hope and Affiliated Gas Companies, Pittsburgh, Pa.): I would like to know the content of any nitrogen and carbon dioxide in the gas in the lines.

DR. ROELEN: We give a guarantee that the increased maximum will be 60 per cent. That is the guarantee which the Ruhrgas Corporation gives—that it will be no more than 60 per cent.

E. A. HAWK (Fuel Engineer, Department of Research and Technology, Tennessee Coal, Iron & Railroad Company, Birmingham, Ala.): What is the most economical velocity for low pressure and high pressure transmission lines?

DR. ROELEN: That is a question of calculating to find the right ratio between the capital investment and the operating cost. The question can be answered generally.

E. E. LUNGREN (Western United Zinc & Electric Company, Aurora, Ill.): We have had some experience with deposits in our lines operating at 75 pounds pressure at distances of possibly eight miles from the plant.

I wonder whether they have had any similar experiences in Germany.

DR. ROELEN: No, only with naphthalene.

CHAIRMAN FULWEILER: Your gas was not coal gas, was it?

MR. LUNGREN: Not in the present case, but we have had some experience with coal gas.

MR. K. B. NAGLER (Peoples Gas, Light and Coke Company, Chicago, Ill.): There are some comments I should like to make, not about the paper, but the gas system itself.

I have been in Germany within the last two months and looked at the Ruhr gas lines from the viewpoint of a United States gas man. I thought I might emphasize some aspects of the system that would not be stressed in a presentation such as the foregoing.

First is the natural question: Who is behind these plans of long distance gas transmission? Some of the units of the interconnected system now building have been in service fifteen to twenty years, on a small scale, and have really

been inter-plant systems. That is, the collieries and their coke plants have had their gas conducted to steel works nearby, all being owned by the same company.

Economics has dictated the forming of an operating company for all of these individual units which have had distribution lines, and so this large company, the Ruhrgas Company, has been formed. One of the consequences of this unification has been that the transportation of the gas, which originally was only for their own steel plants, was extended to some smaller cities in the Ruhr district. Now contracts are being closed with towns along the system, notably the city of Hanover, which has almost a half million population. This last will require a very considerable extension of the present lines.

The fact is, that in spite of connecting many of the Ruhr municipalities into the gas system, of the total gas to be handled, probably as much as 90 per cent will be used by the steel works themselves. So the additional load of these individual towns which are put on these gas lines will not appreciably affect their load factor. To meet hourly peak demands it is contemplated to install large gas holders at both ends of the proposed gas trunk main. The provision seems to be to take certain industries off the lines at such times as there is an interruption of supply, in order to guarantee service in the individual towns that have contracted for the gas, and further than that it is proposed to put in a water gas plant near Cologne as a standby plant.

I think one point about the pipe line that is very interesting is the type of construction which Dr. Roelen described and which, so far as I know, has not been used in this country. The Ruhrgas Company, on account of ground disturbances in the mine districts, have developed a type of sleeve joint which, in essence, is a bell and spigot joint of steel pipe. The spigot end is driven into the steel bell, the long bell being welded around the spigot, in this way the actual bearing area is at the root of the bell, the weld having no strain upon it and requiring to be gas-tight only. Another type of joint, which is a kind of ball joint, permits them to make bends up to 23 degrees. In this the spigot end is upset to form a ring of semicircular section around which the bell end is peened and then welded. In this joint the bearing surface is the enlarged spigot ball-joint.

We inquired how these lines are protected against corrosion and electrolysis and noted that the insulation with bitumen and felt paper was done with exceeding care. The pipes are wrapped at the steel mill and any breaks in the insulation due to handling are carefully repaired before the trench is closed. The welded joints are covered with wrappings soaked in protoparaffin and a layer of straw rope. Where the ground was rocky, the backfill was screened to prevent breaks in the insulation.

Director Peterson told of one job in Galicia, where to prevent electrolytic corrosion, they actually connected some storage batteries to a steel oil line putting a plus potential on it.

The entire pipe line as we saw it, mechanically—and that was the thing we looked after in particular—was extraordinarily well done as a welding job. The river crossings where they laid in the stream bed, were made in duplicate and valved on both sides. The valves are designed for an eventual pressure of four to five hundred pounds for parts of the system. The compressors that

we saw were operating at four or five atmospheres but designed for a future pressure of ten or twelve atmospheres.

Dr. Roelen brought out the subject of oxygen content in the gas to be delivered to the municipalities. The German Gas Association has formulated exceedingly stringent regulations and standards for gas service. Some of their stipulations such as to oxygen content, B.t.u. variation and specific gravity variation are much more closely drawn than any standards that we observe in the United States.

CHAIRMAN FULWEILER: Gentlemen, I feel we have used up all our time in this portion of the section on the discussion of this paper.

I would ask Dr. Roelen if he wishes to say anything further?

If not, we will have to call on the next speaker. The title of the next paper is, "A Study of the Comparative Costs of Gas Production in the Retort House."

Dr. Smith's paper on the comparative costs of producing gas in the retort house, and Mr. Bing's paper are now open for discussion.

H. C. PORTER (Consulting Engineer, Philadelphia, Pa.): There is so much in Dr. Smith's paper that the ordinary mind finds difficulty in grasping it all at once.

There was one figure, however, a general tabulation, that he put on the screen and kept there for some time. It appeared to me as I read that table, that the credit he used there for coke, in comparing the costs, was put at the same figure (22/-) on all types of plants (after making correction for breeze, Dr. Smith says). From the different types of plants it seems to me there is a possibility or even a probability of a lesser return on coke per ton in some cases than in others.

Also in regard to the fuel cost which he brought out as an important item, I would like to ask: Is that fuel cost, that is, the cost of coke used, put in at 22/-, or is it taken as a lesser cost per ton, due to the fact that small-sized coke was used for the producers?

These points make a difference in such comparisons of plants. The American Gas Association, through its carbonization committee, conducted a few years ago a series of tests on different carbonizing plants, and thus obtained cokes from different types of retorts, and these cokes were tested for physical quality at the Bureau of Mines very thoroughly and these results have been published in Reports of the Carbonization Committee, American Gas Association for 1926, 1927 and 1928.

Some of the cokes did not show up as well as others in physical quality, relative amount of breeze and dust, and in bulkiness or weight per cubic foot.

These things have a large effect on the value of the coke, or the coke return from each type of plant, particularly the relative amount of salable coke, and the amount of abrasion or breakage in handling and shipping, which reduces the returns per ton.

I wish I might have a little more explanation of the figures and the table on the basis of those considerations.

DR. SMITH (Technical Director, Woodall-Duckham Companies, London, England): The breeze production in each system was allowed for. In fact, the coke breeze—actual salable coke, apartment coke breeze—brings about an average of 24/- to 25/- a ton. The average price is taken as 22/-.

In regard to the one particular system being able to use more breeze produced than another, in the three systems that I indicated, the type of producer that is available has come to the lot, so the utilization of breeze was not allowed for.

In regard to what coke is used in the producers, this was screen coke with all fines, that is, below a quarter was assumed, because with the larger quantity of breeze, the throughput of the producer is less, the producer had to be bigger, the labor is greater, and it pays to produce a good class of coke in a self-contained producer.

Those points are really as near as possible. Under English conditions, a practical set of figures has been worked out that would not apply to American conditions, because there is no doubt in many places here the soft tar, vertical coke does not bring as high a price, I believe, as nut coke or hard coke, which is horizontal coke. And these figures would not apply the same way. But even here the vertical coke is bringing a good price and is being sold with advantage. With us, the vertical coke brings the highest price. But that is not given credit in the figures.

A. GORDON KING (Service Engineer, American Gas Association, New York City): Dr. Smith's paper is like all his other contributions; it is a distinct addition to the literature of the gas industry.

In using this material, more or less as a yardstick, especially in these days of economic pressure on the gas industry, there are two points I would like to ask Dr. Smith to clear up for me.

One of them, the first, is: What is included in the capital cost of approximately £260, that is, the amount of equipment and how far it goes along the line?

The second is with reference to Table 3, to which Dr. Porter just referred. Would it be a safe assumption, speaking from the point of view of using your material, Dr. Smith, as a yardstick only, to apply your statement that the probable selling price, which was shown as the production cost per therm would be in the neighborhood of about three times such production cost?

DR. SMITH: It is safe to say that in Great Britain and generally, the normal average selling price—that is, taking the whole of the gas of any undertaking and dividing that into the gross receipts from the consumer—that the selling price in Great Britain is at least three times the cost of production of gas in the retort house, including everything.

My very definite point is, and the point I have tried to make in Great Britain, that engineers may throw money about in inefficient methods of maintenance and publicity without much consideration as to whether this form of publicity is ten per cent better than that form of publicity, and they will be stretching all the time for a tenth of a penny per therm, which has no bearing whatever, and is nothing to what can be thrown away in inefficient distribution. The distribution side should have much more attention.

As to capital cost, that includes everything, from coal out of the truck, which is outside the retort house, to coal on the pile without steam, coke on the pile, including everything, retort house, foundations, elevators, wasting boilers, and everything that is necessary for handling the coal from the truck to the coke on the heap. This is in the retort house only, not purification and not cleaning.

F. ZUR NEDDEN: I am speaking somewhat as a layman, and I want to bring out one point that was really underlying all three papers, if you will forgive me, Mr. Chairman, for transversing slightly. I have a special interest in doing so.

The underlying point was this: That really the gas works are for a great part not gas works, but they are also coke works. Along with gas, you must always sell the coke, and in the measure you can sell coke, you may be able to increase your sales of gas.

You are always in between the scissors. You want to make more gas and push the sale of gas by lower price of gas, for instance, or better tariffs. And you will instantaneously have more coke, and unless you can take care of the sale of that coke, your increase in selling gas will not benefit you any.

This is the situation that all the gas works of all the world are in precisely, and this is the point where the long-distance transmission from coke oven plants and the national gas transmission in this country is bringing relief, looking at the thing purely from the standpoint of the utilization of gas, because there we have gases put to the consumption of the public and of industry which do not entail a production of coke at the same time. Especially this is true of natural gas, but as long as it is surplus gas in coke ovens, it applies to coke oven gas, too.

About this point hinges the whole development of the long distance gas transmissions with which dealt the first paper. About this point hinges the price of coke, which Dr. Smith put forward in his paper and which is lower than it is in this country. And from this point hinges what Mr. Bing mentioned, the possibilities of developing an industrial market for gas and the possibilities of introducing your coke oven gas into your gas plants.

This is why I am mentioning this point. We are looking forward to another World Power Conference in 1930. This World Power Conference has for its aim, as Dr. Smith very aptly stated in his lecture at the public meeting on Tuesday night, the economics of power. And it would be extremely valuable if we could have at that occasion, papers very much on the line of that of Dr. Smith's—perhaps one paper taking the same subject from the American point of view, not dealing with costs per therm, but perhaps dealing with costs per cubic foot, something like that, putting the whole story in the American manner. Perhaps we could get another paper putting the whole story in the French or the German ways, which would be very much similar, because the conditions of the industry are very similar in both countries.

Then again we might have another paper which would tell the secret, how gas works are disposing of their coke in the various countries and how they are going to increase industrial use of gas without at the same time getting rid of their coke. That would be a paper that would interest the economist and it would really interest the statesman.

In that way the World Power Conference would fulfill its object of being a mouthpiece of the engineering profession towards the commercialist, towards the business man, the economist, and the statesman.

Therefore, I would put in these few words, in order to ask you to prepare. I hope you will all come to our conference in Berlin in 1930, the World Power Conference, and prepare papers on that line for that specific occasion, because in that way, we will truly derive the greatest benefit from the World Power Conference for the engineering profession and for the gas industry at large.

DR. SMITH: Mr. Chairman, I would ask that for international conferences such as this—I know Mr. zur Nedden will agree that Berlin would have all the advantage—that if our American colleagues do prepare figures of this kind, they should not only put the figures forward as costs per thousand, but in order to make them in any way comparative, they must also be expressed as costs, say per hundred thousand B.t.u. made.

It does not matter whether you call it a therm or decatherm or anything else. They must be comparative, and a statement of results of costs per thousand of 500 B.t.u. gas and costs per thousand of 460 B.t.u. gas is practically of no value. It must be worked back onto a common basis of heat units, whatever you call them.

CHAIRMAN FULWEILER: I wonder if the meeting would permit me to make one suggestion. It has been in my mind for some time.

Why should not the gas industry give their costs in kilowatt hours? We are selling energy, and if you begin to figure costs of gas in kilowatt hours, it makes a marvelous selling point with the electric people.

I did not mean to give the impression to the meeting that only the last two papers are open for discussion. All papers which were read this morning are open for discussion.

I wish to take the opportunity—Dr. Bunte is now here. There were several questions asked during your absence, Dr. Bunte, regarding the composition of the gas that is proposed to distribute. They wish to know generally what is the analysis of the gas it is proposed to distribute by the Ruhrgas Corporation, in particular, how much carbon monoxide, how much oxygen, how much nitrogen, and how much carbon dioxide. Those were the four things about which inquiry was made, and Dr. Roelen intimated that you had made the experiments and would be in a better position to make the proper answer to this question.

Are you prepared to make that answer so that we can have it on record?

DR. CARL BUNTE (Professor, Technische Hochschule, Karlsruhe, Germany. Remarks translated by Mr. Zur Nedden):

The Ruhrgas Company or Corporation has so far tried not to be put on record as regards the contents of inert gases in the gas it distributes. It has always tried to make contracts in such shape that they could evade the necessity of being put on record on the content of inert gases.

The gas industry now claims and wants in Germany that there should be a certain, or almost as complete as possible, uniformity in the properties of the

gas which comes through the long distance line from the coke ovens into the towns and of the gas that is made within the towns.

Now in the comparison between these two gases and between any two gases for burning purposes, there enter as principal factors the contents in hydrogen, the specific gravity, and the limiting of value, the upper limit of the percentage of inert gases.

The gas works have so far in Germany put forward the claim that the percentage of nitrogen plus carbon dioxide should not exceed in any case 15 per cent, and if possible, be always kept at about 12 per cent or lower.

The contents in carbon dioxide were not especially limited, because the difference in the bearing of carbon dioxide and of nitrogen is very small. So it is quite sufficient to make the limit the sum of nitrogen plus carbon dioxide.

As regards the contents in carbon monoxide, there is no special restriction, and Professor Bunte says, "happily so," because it has been shown in France that the restriction in contents of carbon monoxide is rather working against progress of the industry.

Again there would enter the question of naphthalene contents. The gas works do not stress this point, because they have no particular difficulties with naphthalene, but they think that the Ruhrgas Company would have every reason to be very careful as regards naphthalene contents, because when compressing gases, the naphthalene makes trouble in direct proportion to the pressure drive.

Therefore, the Ruhrgas Company would have to see to it themselves that the naphthalene content should not be too high, because otherwise they would get into difficulties when compressing the gas. After the gas is released from the high pressure, there would be no difficulty with naphthalene once the naphthalene has not given any difficulties under high pressure.

Professor Bunte states: The Ruhrgas Corporation seems to be rather optimistic in regard to the naphthalene question. He does not know whether they are right.

Professor Bunte further wanted to add something to the discussion. He said that in general, the big gas works in Germany have a rule for the calorific value of the gas around 480 B.t.u. per cubic foot. They make it a point that not only the calorific value but also at the same time the specific gravity of the gas should be in a certain harmony.

In other words, they do not put forward the absolute calorific value, but rather the fraction represented by the calorific value divided by the square root of the specific gravity, because this factor hydrogen, or carbon, if you may term the calorific value, divided by the square root of  $S$ , the specific gravity, is the value which governs the efflux of the quantity of therms per second out of a given orifice.

Therefore, when you want to keep all your burners in the system that depends on the special gas works in order constantly, the above value should be kept constant. Otherwise you would have to readjust the burners and come to constantly varying proportions between the oxygen and the air and the number of therms going through the orifice of the given nozzle per second or per minute.

Professor Bunte points out that the worst difficulty in trying to get at the

true and just comparison between the two gases which come from two different sources is one point which is not readily settled by a simple formula such as  $H + S\frac{1}{2}$ . It is with regard to the characteristics of flame propagation.

Flame propagation will depend on various factors. It is not quite possible to predict this behavior from a given analysis of the gas. It seems to be established that an increase in hydrogen will improve flame propagation while an increase in carbon dioxide and carbon monoxide will reduce flame propagation.

Now here seems to be something which will have to be overcome in order fairly to compare two gases that come from different sources. For instance if the Ruhr gas, the long distance gas, would be taken from the coke ovens in such a way that the gas is taken from the coke ovens during the lower period of the gas production, rather than from the beginning to the end of the gas production in the coke ovens, then it would be comparatively rich in hydrogen, and on account of that richness in hydrogen, it might then perhaps be allowed to be a little richer in inert gases, because hydrogen would give good flame propagation and inert gases would again reduce the flame propagation, and it might work out to the same end at last.

The contents in hydrogen of coke oven gas, taken over the whole period of making coke, Professor Bunte puts at something like 60 per cent. It might be even a little higher.

I think that is about all you said, Professor Bunte.

CHAIRMAN FULWEILER: Is there any further discussion on any of the three papers which have been presented this morning?

Dr. Bunte, there was a question raised by the gentleman from the natural gas industry, regarding the possible effect of the high pressure of the oxygen in forming carbonyl, in content with the iron of the mains, and whether this might not be decomposed, thus giving rise to dust which would thus be carried on.

Dr. Bunte answered in German.

MR. ZUR NEDDEN (Translating DR. BUNTE's remarks): Professor Bunte states he does not think that oxygen is the real source of carbonyl. He pointed out that it is quite possible to have 100 per cent oxygen in steel flasks without anything detrimental resulting.

But oxygen might become dangerous or obnoxious at the moment when there are liquid condensations or water present.

There might be a misunderstanding in so far as carbonyl, ferrocabonyl, would perhaps be produced by the influence of carbon monoxide. That seems to be an established fact, and it would have to be studied very carefully in long distance transmission of gas.

Professor Bunte quoted the case of one of the German chemical works where they tried to technically manufacture ferrocabonyl and carbonyl iron. These studies have given very valuable hints as to what probably might happen.

On the other side, some studies are made in connection with compressed gas for railroad cars, which seem to point to the possibility of the iron of the containers, after a certain pressure has been reached, ceasing to form carbonyl. It becomes immunized.

The man who has tested these things is Professor Terres, who read a paper here, and he is a very reliable experimenter, so it seems very probable that this study was right.

Probably if one studies the subject of the formation of ferrocabonyl there might be some difficulties in the beginning, but later on, one would probably overcome them.

CHAIRMAN FULWEILER: I must apologize to the meeting. I made that mistake. I started with two thoughts in mind—first that the oxygen would form iron oxide, which would also form dust, and secondly, that the carbon monoxide would form iron carbonyl.

Unfortunately, I put them at the same time, but Dr. Bunte has corrected the mistake.

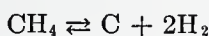
# THE FORMATION OF BENZOL AND OTHER HYDROCARBONS BY THE ACTION OF HEAT ON METHANE

By FRANZ FISCHER

BASED ON EXPERIMENTS CONDUCTED IN COLLABORATION WITH H. PICHLER, K. MEYER, AND H. KOCH

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The decomposition of pure methane by the action of heat yields according to information in scientific literature, carbon and hydrogen according to the equation



In the presence of catalyzers as nickel, cobalt, and iron the equilibrium point is more quickly reached. Figure 1 shows the different positions of the equilibrium found for different temperatures by Mayer and Altmayer.<sup>1</sup> From this we can see that at 850°C. on reaching equilibrium the methane is almost completely decomposed into carbon and hydrogen.

Bone and Coward<sup>2</sup> investigated the thermal decomposition of methane at different temperatures in a porcelain tube without the presence of a special catalyzer, and they also obtain the result that methane is decomposed substantially into carbon and hydrogen. However, their work contains hints from which we can conclude that when methane is decomposed, even if in very small quantities, there may arise other products in addition to carbon and hydrogen depending on the conditions of the experiment. Table I shows the results of five experiments, in which methane was heated in a closed porcelain tube to about 1000° for different periods of time.

Bone and Coward point to the fact that the formation of acetylene or of unsaturated hydrocarbons could be discovered only in the experiments in which the methane concentration at the end amounted to more than 60 per cent, and that upon a further reduction of the methane concentration the gas in contact with the hot walls continued to decompose directly into its elements. Bone and Coward add that in harmony with the above, there was an indication of the

<sup>1</sup> *Ber. Dtsch. chem. Ges.*, 40, 2134 (1907); *Journ. f. Gasbeleuchtung*, 52, 238 (1909).

<sup>2</sup> *Journ. chem. Soc. London*, 93, 1197 (1908).

formation of aromatic hydrocarbons only in case of a high methane concentration from the fact that a light vapor appeared when the gas which had been heated came out of the cooling coil.

Bone and Coward give no information concerning the fact that aromatic combinations were detected, or concerning a quantitative determination of their mass.

W. C. Slater<sup>3</sup> investigated the influence of surfaces of different materials on the decomposition velocity of methane at 910°. He found that quartz, aluminum oxide, magnesium oxide, and barium oxide

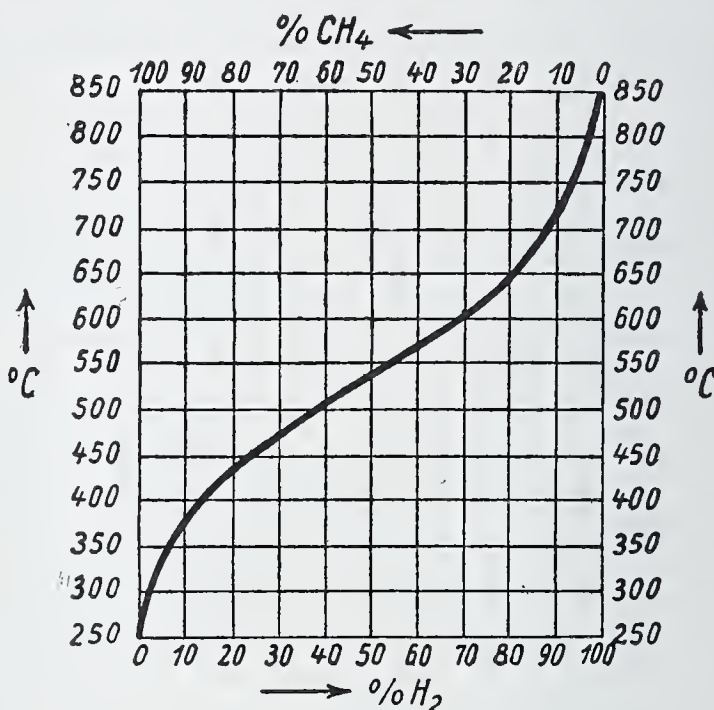


FIG. 1

did not materially accelerate decomposition, while wood charcoal, graphite, carborundum, iron, and copper did. He had the methane enclosed in a porcelain tube; the gas was heated five minutes at a time, and then the degree of decomposition was determined. Slater mentions emphatically that the remaining gas contained nothing but methane, hydrogen and a trace of nitrogen.

R. C. Cartelo<sup>4</sup> also investigated the thermal decomposition of me-

<sup>3</sup> *Journ. chem. Soc.*, 109, 160 (1916).

<sup>4</sup> *Journ. physical. Chem.*, 28, 1036 (1924).

thane. He arrives at results varying somewhat from those of Mayer and Altmayer, and calculates according to the Nernst formula the equilibrium concentrations of ethylene and of acetylene which may be formed by the separation of hydrogen from methane and the union of two residues. These amounts are exceedingly small.

In older literature one finds, however, occasional references concerning the occurrence of other hydrocarbons, when methane is decomposed by heat. Berthelot,<sup>5</sup> and before him, others, found that when methane is passed slowly through faintly glowing porcelain tubes, traces of naphthalene are formed, which, however, were not determined quantitatively. Berthelot<sup>6</sup> also mentions that he proved qualitatively the occurrence of traces of benzol. He passed several

TABLE 1

	DURATION OF HEATING				
	1 minute	5 minutes	15 minutes	30 minutes	60 minutes
	Composition of the reaction gases in volume per cent				
C <sub>2</sub> H <sub>2</sub> .....	0.5	0.5	0	0	0
Heavy H. C.....	0.3	0.5	1.3	0.35	0
CH <sub>4</sub> .....	90.4	75.4	65.25	62.85	48.2
H <sub>2</sub> .....	8.8	23.6	33.3	36.8	51.2

liters of methane through a red hot tube, and led the escaping gas through fuming nitric acid. He proved the formation of traces of nitrobenzene by reduction to aniline and the identification of the latter by color reactions. He did not isolate either nitro-benzene or aniline as such, but there is no doubt, as we shall see later, as to the correctness of his observations.<sup>7</sup> He expresses the opinion that benzene and naphthalene were formed from traces of acetylene, which in its turn originated from the methane at red heat.

The occurrence of small quantities of naphthalene has certainly also been observed since that time, and former collaborators and myself have detected it on several occasions.<sup>8</sup> But only a little while

<sup>5</sup> Berthelot, *Les Carbures d'Hydrogene*, p. 34, 36.

<sup>6</sup> Berthelot, *Les Carbures d'Hydrogene*, p. 34.

<sup>7</sup> The supposition that benzene and traces of naphthalene are formed from homologs of methane (which are easily decomposed by heat) does not prove correct.

<sup>8</sup> Franz Fischer and Hans Tropsch, *Brennstoff-Chemie*, 9, 39 (1928).

ago did the opportunity present itself for a more thorough study of the conditions under which hydrocarbons, rather than carbon and hydrogen,<sup>9</sup> appear as the product of the thermal decomposition of methane. It was to be determined whether it were possible by changing the conditions of the experiment, to produce larger quantities of unsaturated and aromatic hydrocarbons by the decomposition of methane, instead of the traces mentioned before. Methane alone and not its homologs were to be examined. The thermal decomposability of the latter is already well known. Further, the decomposition of methane below 1,200° was to be studied, that is, at temperatures which were easily attainable without the use of electrical energy. Moreover, the formation of acetylene out of methane in the electric arc has been known for some time.

In the thermal decomposition of methane flowing through a tube it could be conceived that by shortening the period of heating, the complete separation of the hydrogen from a methane molecule could be prevented, so that unstable groups such as CH<sub>3</sub>, CH<sub>2</sub>, or CH appear temporarily, and then would associate in some way or polymerize. In this work I was aided by knowledge gained in previous years in a series of experiments on the formation of ozone, hydrogen peroxide and nitric oxide at high temperature; here the cooling rate was of the greatest importance.<sup>10</sup> I believed that this should be true also in the study of the thermal decomposition of methane.

From this point of view, it seemed clear that the flowing velocity, or in other words, the duration of heating, must be of just as great importance in the formation of larger quantities of hydrocarbons, as the temperature of heating. For this reason we conducted numerous experiments on the influence of the duration of heating; experiments on the influence of the velocity of cooling are to follow at a later time. We have, on the other hand, already paid attention to the importance of catalyzers, as well as to a number of other factors.

<sup>9</sup> Quite recently there appeared in the magazine *Fuel*, 7, 397 (1928) a review of the literature on the hitherto prevailing chemical utilization of methane, by Nash and Stanley, which points to the fact of how little is known concerning the thermal or catalytic transformation of methane. This paper will, doubtless, fill this gap for a part.

<sup>10</sup> Franz Fischer u. F. Braehmer, *Ber. Dtsch. chem. Ges.*, 39, 940 (1906).

Franz Fischer u. H. Marx, *Ber. Dtsch. chem. Ges.* 39, 2557 (1906).

*Chem. Ztg.*, 30, 1291 (1906).

## EXPERIMENTAL PART

1. *Experimental Apparatus*

Figure 2 shows the arrangement of the apparatus used in our first experiments.

The gas which was led from a cylinder or from a gasometer, passed at 1 through a meter to measure the amount entering the furnace. In the figure, 2 is a Mars oven 22 cm. long, which was heated by Silite rods. The temperature was measured at the middle of the oven on the outer wall of the reaction tube with a Platinum-platinumrhodium thermoelectric element, as this is customary in case of Mars ovens.<sup>11</sup> The length of the glow filament of the heating rod was 15 cm., so that about 10 cm. of the rod length was considered as the zone of reaction. The escaping gas was cleared electrically from the tar

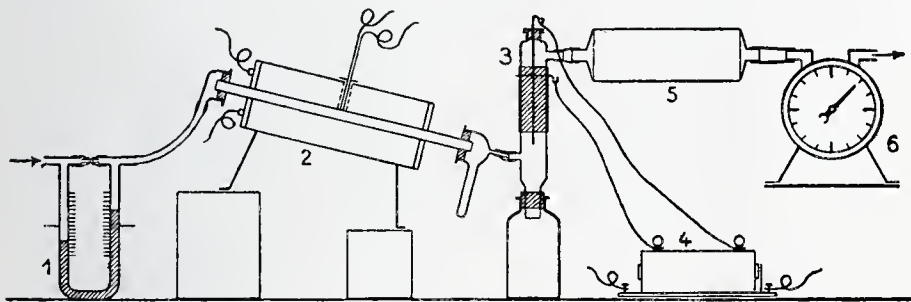


FIG. 2

vapors at 3. The tar separator consisted of a Liebig condenser jacket which the gas entered from below. A sheet of tin-foil on the outer side of the jacket was connected with the one pole of a powerful inductor 4; a copper wire passing through the center of the condenser was attached to the other pole. We were thus able to precipitate the vapors of the gases even at great velocities. After the electrostatic purification, the gas was conducted at 5 through a receptacle containing activated carbon for absorption of the light oils still present. In the figure, 6 is a gas meter that measures the escaping gases so that a calculation of the expansion can be made.

<sup>11</sup> The interior temperatures are little lower at a gas velocity of 4 liters, identical with that measured on the outside; up to 70 liters per hour they were 20° lower.

2. *Experiments in a Tube of Large Diameter*

Table II shows experiments in which methane<sup>12</sup> was passed at various speeds through a porcelain tube, 16 mm. in diameter. With a gas velocity of 4 liters per hour and a tube temperature a little below 900°, there began to appear in the escaping gas a slight amount of vapor, and an expansion of 3 per cent was measured. With rising temperature the formation of vapors rapidly increased; their color which was whitish at the beginning, became darker, and

TABLE II

NUMBER	GAS BEFORE THE EXPERIMENT, °C.							
	Heavy H. C.	H <sub>2</sub>	CH <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	Tempera- ture °C.	Time <i>hours</i>	Liters per hour	Exp. <i>per cent</i>
1	1.8	0.0	93.0	0.0	900	—	4	3
2	—	—	—	—	975	—	4	12
3	—	—	—	—	1,000	—	3.85	19
4	—	—	—	—	1,050	4	70	6
5	—	—	—	—	1,100	4	70	10
6	—	—	—	—	1,150	1½	70	21

NUMBER	GAS AFTER THE EXPERIMENT						
	Heavy H. C.	H <sub>2</sub>	CH <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	Oil	Tar	C
1	—	—	—	—	—	—	—
2	2.8	23.0	66.5	0.0	—	—	—
3	2.7	39.3	55.0	0.0	—	—	—
4	2.6	12.6	79.7	0.0	6.5 g.	1.6 g.	Very little
5	3.4	14.7	77.5	0.0	9.0 g.	4.5 g.	1.0 g.
6	4.2	41.8	50.4	0.0	4.2 g.	3.5 g.	3.1 g.

at 950° it was dark brown. Above this temperature the formation of oil and tar decreased and that of carbon increased, which could be easily observed in the color of the vapors. At the same time the gas smelled strongly of naphthalene, and naphthalene crystals were deposited in the receivers. At 975° the expansion amounted to 12 per cent; at 1000°, 19 per cent. Black clouds of soot had taken the

<sup>12</sup> Furnished by the Concordia Bergbau A. G. in Oberhausen, Rhineland. The methane R was produced by the fractioning of coking gas according to Linde. For analysis, see Table II.

place of the tar vapor and the former clogged the tube after some time.

In order to prevent the decomposition of the methane into carbon and hydrogen, we increased the velocity of the gases passing through the heated tube. At a constant temperature the vapor immediately began to become clearer, and the formation of soot occurring in considerable amounts at  $1000^{\circ}$  stopped immediately. At 70 liters an hour we obtained at  $1,050^{\circ}$  an expansion of 6 per cent, and in four hours, 6.5 grams light oil, 1.6 grams tar, and but very little carbon was deposited on the walls of the tube. At  $1,100^{\circ}$  to  $1,110^{\circ}$  the expansion varied from 10 to 11 per cent. In four hours, 9 grams oil, 4.5 grams tar and 1 gram carbon were formed. The vapors were again somewhat darker than in experiment 4, which was also borne out in the ratio of the oil to the tar; however, no soot was found in the gases leaving the reaction tube. Upon a further increase in temperature the color of the vapors passed through various shades of brown and became black, which was to be attributed to the above mentioned formation of soot. At  $1,150^{\circ}$  to  $1,160^{\circ}$  (experiment 6) the expansion was 21 to 22 per cent. In one hour and 40 minutes 4.2 grams oil, 3.5 grams tar, and 3.1 grams carbon were formed. After one and three-fourths hours the tube was completely clogged by voluminous soot formation.

Thus the first experiments showed: (1) that a relatively high temperature is required to attain a satisfactory yield; (2) that with rising temperature the appearance of free carbon increases rapidly; (3) that this undesirable decomposition can be prevented by a suitable increase in velocity of the gas.

### *3. Capillary Experiments*

The necessity of having to use high gas velocities in order to work against the decomposition of the methane into carbon and hydrogen, induced us to use reaction tubes with the least possible cross section. In the experiments 1 to 3 of Table III we used porcelain tubes having 5 mm. or even 4 mm. for their inside diameter. Here (experiment 1) a yield in oil plus tar equal to 12 per cent of the weight of the methane put through was reached. Corresponding to the smaller cross section of the tubes ( $19\text{ mm.}^2$  to  $47\text{ mm.}^2$  in the double tube and  $201\text{ mm.}^2$  in the wide porcelain tube) less gas was put through in these experiments. In experiments 4 and 5 a quartz capillary tube was used. It was proved that quartz does not accelerate the decomposi-

TABLE III  
 RESULTING GAS: "CONCORDIA METHANE"

NUMBER	TUBE, INSIDE DIAMETER	TEMPER- ATURE	TIME	LITERS PER HOUR	EXP.	HEAVY H.C.	H <sub>2</sub>	CH <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	OIL TAR	C
		°C.	hours		per cent						
1	Porel. gl. 5 mm.	1,090	1	13.0	—	—	—	—	—	1 g. = 12% of CH <sub>4</sub>	—
2	Porel. gl.	1,090	2 $\frac{1}{4}$	20.7	—	—	—	—	—	3 g.	—
3	Porel. ungl. 4 mm.	1,040	4	6.5	14.6	—	—	—	—	1.4 g. = 8.8% of CH <sub>4</sub>	—
4	Quartz, 3 mm.	1,130	2 $\frac{1}{2}$	6.5	17.4	—	—	—	—	1.0 g. = 10% of CH <sub>4</sub>	—
5	2 Quartz to 3 mm.	1,130	3 $\frac{1}{3}$	12.9	21.0	3.2	31.5	59.5	0.0	3.4 g. = 12.9% of CH <sub>4</sub>	—

tion of  $\text{CH}_4$  into C and  $\text{H}_2$ , but makes possible the collection of the by-products desired by us. In experiment 5 the yield in oil and tar amounted to 12.9 per cent of the methane.

#### *4. The Influence of the Tube Material and of Catalysts*

In the course of our investigations we found that the material of the tube had a considerable influence on the direction of the reaction. In using tubes of Marquard paste (Marquard-Masse), for example, it was established that the decomposition of methane into carbon and hydrogen is favored. Berlin hard porcelains and quartz were best suited as materials for our reaction tubes. Starting with the intention of keeping the reaction temperature as low as possible, we investigated also the influence of different catalysts.

In several experiments a thin porcelain tube, 5.5 mm. in diameter was used, into which an iron wire, 2 mm. in diameter was laid. The iron caused a somewhat higher yield but this resulted in an increase in the separation of carbon; the effect of copper was similar but not so marked. In several other experiments the influence of tungsten wire or of molybdenum wire was tested. Both these metals in wire form showed no catalytic influence. At another time an iron boat that contained caustic potash was pushed into the porcelain tube, and methane was passed over it at different temperatures. In this case at  $650^\circ$  a strong decomposition set in. The gas produced at this temperature contained 4.6 per cent  $\text{H}_2$ ; at  $750^\circ$ , 10 per cent; at  $1000^\circ$ , 56 per cent. Neither oil nor tar was formed, but, on the contrary, abundant quantities of carbon. Let us mention several further observations: graphite accelerates the separation of carbon; however, tin and silica-gel do not.

The influence of a preliminary treatment of the porcelain tube on its catalytic behavior was also investigated. Preliminary treatment with gaseous hydrochloric acid and treatment with boric acid or hydrofluoric acid showed no noticeable influence.

#### *5. The Influence of the Composition of the Gas*

In our experiments we investigated examples of methane of different origins and purity as well as mixtures with other gases. Table IV gives an outline. The experiments were conducted, partly in narrow porcelain tubes and in narrow quartz tubes, partly also in double tubes, which were constructed in such a way that a closed porcelain tube with an exterior diameter of 14 mm. was pushed into

TABLE IV

NUMBER	TUBE, INSIDE DIAMETER	GAS BEFORE THE EXPERIMENT. NAME	HEAVY H. C.	H <sub>2</sub>	CH <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	TEMPERATURE °C.	TIME hours	LITERS PER HOUR	EXP. per cent	GAS AFTER EXPERIMENT				OIL	TAR	C
											Heavy H. C.	H <sub>2</sub>	CH <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>			
1	Double tube	Concordia	1.8	0.0	93.0	0.0	1,100	6	68	6.5	2.4	14.4	78.2	0.0	6 cc.	3 g.	1 g.
2	Porcl. 5 mm.	Concordia washed with fuming H <sub>2</sub> SO <sub>4</sub>	0.6	0.0	93.8	0.0	1,100	—	6.5	21	2.6	21.8	71.8	0.0	—	—	—
3	Double tube	Neuegamme	0.3	0.2	89.0	0.0	1,085	5½	63	6	1.3	11.4	76.6	—	7 g.	3 g.	0.2 g.
4	Porcl. 14 mm.	CH <sub>4</sub> prepared from Al <sub>2</sub> C <sub>3</sub>	0.0	0.0	91.6	0.0	1,110	3	60	—	—	—	—	—	3 g.	0.5 g.	—
5	Porcl. 5 mm	CH <sub>4</sub> prepared from Al <sub>2</sub> C <sub>3</sub>	0.0	9.2	83.0	0.0	1,190	4½	24	About 8	3.0	29.8	61.8	0.0	5.7 g.	1.1 g.	Very little
6	Double tube	Fermentation methane	0.5	0.0	91.3	0.0	1,110	6	63	About 6	1.5	11.0	82.2	0.0	5 g.	2 g.	Little
7	Porcl. 5.5 mm	CH <sub>4</sub> from illum. water gas mix- ture after Sabatier	0.0	4.0	67.7	0.0	1,150	—	30	4.5	—	—	—	—	—	—	—
8	2 Quartz to 3 mm.	Gas by mixture of H <sub>2</sub> and CH <sub>4</sub>	0.7	66.7	26.7	0.0	1,200	2½	12.9	—	2.4	72.2	14.3	0.0	0.7 g.	0.7 g.	—
9	2 Quartz to 3 mm.	Reaction gas Tab. III, ex 5	3.2	31.5	59.5	0.0	1,190	—	12.9	24.6	1.5	54.7	34.0	0.0	—	—	—

a porcelain tube that had an interior diameter of 16 mm. The gas passed through the narrow intervening space.

Purified Concordia methane, methane from the Neuengamme gas well near Hamburg, as well as a gas coming from the Emschergerossenschaft which had resulted from fermentation, behaved like the methane of Concordia in Oberhausen used for the rest of the experiments. In experiment 5 we used methane made from aluminium carbide which was free from all other hydrocarbons. Here the especially favorable ratio of light oil to tar is noteworthy under the conditions chosen.

Illuminating gas with only 23 per cent  $\text{CH}_4$  showed also the characteristic formation of vapors, but at a somewhat higher temperature. This is also true of an experiment in which hydrogen and methane were mixed in about the ratio of 3:1, and of a gas that had already reacted once and was passed for a second time through the heated tube.

A comparison of the behavior of the individual kinds of methane with analogous experiments described before, showed no essential differences. If methane is diluted with other gases then the reaction temperature must be raised if it is desired to obtain the same methane transformation. This fact could be especially well observed in experiments where under certain conditions pure methane gave off brown vapors, and upon the addition of nitrogen, carbon monoxide, or carbon dioxide, the vapors cleared up at once. If the temperature was raised somewhat, then in all cases, in spite of the presence of the mentioned gases, the formation of vapors began, i.e., formation of oil and tar started.

### *6. Investigation of the Products Obtained*

To manufacture a larger quantity of light oils and tar long runs were conducted at  $1,100^\circ$  with a gas throughput of 60 to 70 liters per hour. After forty-eight hours none of the tubes were clogged with carbon. These runs yielded a rather watery tar and 140 to 150 ccm. of light oil which were used in the following investigations.

*a. Carbon.* The nature of the carbon arising as a by-product is dependent on the choice of the conditions of the experiment. While in case of low gas velocity, chiefly a soot-like, voluminous, light carbon forms, in the case of high velocity, as for example in the long runs just described, it is hard and sticks tightly to the tube walls in the form of juxtaposed sheets. In experiments where the action of

tin was investigated, the carbon formed peculiar threads looking like cobwebs, while in the first tests with slow gas flow (Table II, experiments 1-3), a carbon with the metallic luster described by Hofmann<sup>13</sup> was produced.

*b. Tar.* The tar held back in the electrostatic gas purifier was brownish black, thinly liquid, lighter than water, smelled distinctly like naphthalene and contained, depending upon the conditions of the experiment, more or less free carbon. When a sample was distilled, it began to boil at about 200°. The distillate (14 per cent) which passed over up to 250°, solidified completely. It consisted chiefly of naphthalene. Of the fraction 250° to 360° (29 per cent), 90 per cent consisted of a yellow-brown, green fluorescent oil; the rest consisted of solid, cyclic hydrocarbons from which anthracene was isolated. The distillation residue was a pitchy substance.

*c. Light Oil.* As mentioned at the beginning, the light oils were recovered by means of activated carbon. After driving them off with superheated steam, we obtained an oil of the following properties:

Density at ordinary room temperature:  $d_4^{25.5} = 0.8724$

Refraction index:  $n_d^{25.3} = 1.50088$

Elementary analysis: 91.72 per cent C and 7.68 per cent H<sub>2</sub>, or  
91.72 per cent C and 7.71 per cent H<sub>2</sub>

Iodine number after Wijs: 58.4 (57.8),

Distillation analysis after Engler and Ubbelohde:

Initial boiling point, 59°:

To °C.	70	80	90	100	110	120	130	140
Volume per cent	3.3	15	48	66	77	79	80	82

To °C.	150	160	170	180	190	200
Volume per cent	83	85	86	87	87	90

A fractional distillation with a column having porcelain rings filled to a height of 30 cm. resulted as follows:

	FRACTION	WEIGHT
		<i>per cent</i>
1	Up to 55°C.	7.8
2	55- 85°	61.1
3	85-115°	12.6
4	115-145°	3.9
5	Over 145°	14.6

<sup>13</sup> *Ber. Dtsch. chem. Ges.*, 56, 2071 (1923); 59, 2433 (1926).

Apparently the first fraction consists chiefly of unsaturated combinations. They add bromine and react with mercuric acetate solution.

The second fraction, which was by far the largest, consisted chiefly of benzene. Upon repeated fractionation 81 per cent passed over between 79° and 81°. The physical constants of this part were determined.

$$D_4^{20} = 0.8750; n_D^{20} = 1.49890$$

The corresponding values for benzene are:

$$D_4^{20} = 0.8736; n_D^{20} = 0.50154$$

Upon nitrating a small quantity, m-dinitro-benzene was obtained amounting to 82 per cent of the theoretical.

The parts boiling above the benzene fraction, as we have already mentioned, decrease in quantity. On the basis of the results obtained from further fractionation, the toluene fraction constitutes approximately 8 per cent of the total light oil, while the xylene fraction amounts to 9 per cent and the naphthalene to 10 per cent. For the detection of toluene, a part was nitrated and 2,4-dinitro-toluene of melting point 70° was obtained with a yield of 74 per cent.

*d. Gas.* As to the composition of the final gases we can refer you to the analyses given in the tables. Among the unsaturated hydrocarbons whose nature we have not yet determined separately, we found acetylene, which was identified by means of the copper compound.

#### DISCUSSION OF THE RESULTS OF THE EXPERIMENTS

The above described experiments have confirmed the supposition that for the production of higher hydrocarbons by way of the thermal decomposition of methane, the duration of the heating is of just as great an importance as the temperature. If the duration of heating exceeds sixty seconds, there is usually time enough to separate all the hydrogen from the methane molecule.<sup>14</sup> The methane decomposes, then, according to the well-known equation




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<sup>14</sup> Whether in a coke oven, benzol develops from methane, we shall discuss in detail at another time.

As far as the temperature is concerned, we observed in the porcelain tubes below  $900^{\circ}\text{C}.$ , without the use of catalyzers no remarkable decomposition of methane even at low velocity. A temperature of  $1,200^{\circ}$  in case of all the velocities (up to 70 liters per hour) investigated by us, was too high for the purposes in mind. Above this temperature there was always an abundant separation of carbon which clogged the tube in a short time. This observation, however, is true only for pure methane. The more it is diluted by inert gases during the reaction, the higher the temperature that must be chosen. Moreover, the influence of the temperature is not a simple matter. There is, certainly, an optimum temperature for the splitting up of the methane and another for the combination of the fragments. Coming to the discussion of the duration of heating, there is, certainly, in an analogous manner, also a most favorable period of heating for a definite temperature of cleavage and a most favorable period of heating for that temperature at which the fragments are to unite to form higher hydrocarbons. The nature of the resulting products will depend upon the radicals to which the methane molecule is decomposed by hydrogen cleavage, and upon what conditions the radicals can combine, so that the total process is surely very complicated, although it may seem to be simply conducted by passing methane through a red hot porcelain tube. But these various factors influenced to a great extent the nature of the products and their relative amounts. To give an example let us mention that in experiment 5, Table IV, which was conducted with methane from aluminum carbide (the methane was only 83 per cent pure since it still contained hydrogen and nitrogen); there was used a porcelain tube 5 mm. in diameter, which was heated for a distance of about 10 cm., and the gas passed through at the rate of 24 liters per hour; here the heating period of the gas amounted to somewhat less than  $\frac{1}{3}$  second. If this heating period be compared with those that were used by Bone and Coward (Table I), it will be seen that in that case the shortest periods were still one hundred and eighty times as long as those used by us, and it can be understood why with them the methane had time to decompose almost entirely into carbon and hydrogen.

If the temperature is carried higher, then the period of heating can be shortened, but the nature of the products will be changed thereby, and the danger of carbon separation becomes greater. Concerning the influence of the velocity of cooling or of the cooling of the

escaping gases, we have not, as yet, conducted any experiments. We plan to conduct investigations concerning this fact and concerning the decomposition of the oil products when the methane decomposes into two separate individually controllable phases.

As far as the rôle of catalyzers for methane cleavage is concerned, they appear to be unsuitable according to our present results, if the separation of carbon is to be prevented. But during the cooling of the gas they can play a rôle by influencing the polymerization of the radicals or low molecular compounds resulting from the methane.

Concerning the rôle of pressure, we can predict with considerable certainty that it is disadvantageous for the methane cleavage itself, but that it will be advantageous for the polymerization of the resulting products. Thus it could be imagined that the best method of going, for example, from methane to benzene, is that the cleavage be carried out under low pressure and that the further treatment of the gas take place under pressure.

Let us refer, by way of example, to experiment 5 of Table IV in discussing the yields obtained by us. This experiment has been especially mentioned already in connection with the period of heating. It was carried out with methane prepared from aluminum carbide. The gas contained 83 per cent methane, 9.2 per cent hydrogen, and the rest was nitrogen. Altogether 108 liters of gas were passed through a porcelain tube with an inner diameter of 5 mm. in  $4\frac{1}{2}$  hours. In this amount are contained 90 liters of pure methane. There were received 5.7 grams of light oils, 1.1 grams of tar, and 3.5 liters of unsaturated hydrocarbons, which calculated as ethylene, weigh 3.7 grams. If these numbers holding good for 90 liters of pure methane are referred to 1 cbm., then we have per cbm. 63 grams of light oils, 12 grams of tar, and 41 grams of ethylene, making a total of 116 grams of higher hydrocarbons. These yields according to our opinion will be considerably improved, which is evident from the fact that of the methane employed only a slight amount was consumed. In the gas employed were 90 liters of pure methane. The quantity of the final gas due to expansion amounted to 118 liters, with a methane content of 61.8 per cent; the remaining methane amounted, accordingly, to 73 liters. Thus 17 liters of methane = 12 grams were used up. If we compare with this weight the sum of the products obtained, namely:  $5.7 + 1.1 + 3.7 = 10.5$  grams, then there is a sufficient agreement if we consider the hydrogen cleavage, for the 25 liters of hydrogen which were formed by cleavage, represent a weight

of about 2 grams. We see from this that no noteworthy amounts of carbon could have separated under the conditions of this experiment.

That at least half of the light oil consists of benzene, has already been shown in the experimental part. Apparently also the other liquid hydrocarbons are chiefly of an aromatic nature, so that it is not impossible, when the conditions are favorable, to resort to methane in benzene synthesis. For example, this may be the case in many countries, where there is no sufficient use for the natural gas present, where so far, on account of the lack of a better use, the so-called carbon black is wastefully manufactured with a yield of only 2 per cent. If the yields were successfully improved, then methane could be considered in the manufacture of benzene, also in the case, where it is produced in the manufacture of a nitrogen-hydrogen mixture suitable for ammonium synthesis, by the fractionating of coke oven gas according to the Linde process, and where it has no other use except to add it to other illuminating gas.

In conclusion it seems fitting also to consider the patent literature on the thermal decomposition of methane on the basis of the information obtained. I have already mentioned that Nash and Stanley collected a bibliography, and pointed out the fact that all the classical works in science had arrived at the result that the chief reaction in methane decomposition is the formation of carbon and hydrogen, but that the contents of the patents issued up to the present do not exactly correspond to this fact.<sup>15</sup>

Among the patents coming in question here, the English patent No. 255,493 with the priority of July 18, 1925, is doubtless the first. This patent of Spindler relates to the transformation of methane into petroleum-like hydrocarbons, and operates in the following way. Methane or gas containing methane is heated from 500° to 950° (presumably to the latter temperature). In doing this the hydrogen is to be partly separated. For the maintaining of such a dissociation the gas is cooled, and then at about 250° to 350° passed over a catalyzer, which contains zinc chloride, which is to bring about a polymerization into petroleum hydrocarbons of the gases resulting from the methane through loss of hydrogen. Both processes, the heating of the methane and the catalysis, are to be accomplished under a pressure of at least 70 atmospheres.

<sup>15</sup> Concerning the theoretical side of benzol production from methane see Alred W. Francis, *Ind. Engin. Chem.*, 20, 277 (1928).

An application for a patent of the Compagnie de Bethune dates from July 27, 1925. The French patent with the number 613,542 describes a process according to which, at a temperature between 200° and 600°, in the presence of catalyzers and under pressure, methane is to be transformed into petroleum. The low temperatures given seem somewhat improbable. It is interesting, however, that the Compagnie de Bethune applied for a patent in France on October 3, 1925, which bears the number 615,972, and which states that if one wants to work with pure methane, it is necessary to add oxygen to the methane in order to produce petroleum hydrocarbons, and that this addition could be made during the catalysis or before then. Moreover, the process is carried out under pressure with a catalyzer consisting of metallic oxides, and at a temperature between 200° and 600°. With respect to the rôle played by the oxygen, one can imagine that it is to react with the methane at these temperatures first to form carbon monoxide and hydrogen, and that with the gas so obtained a kind of benedine synthesis is to be undertaken.

The English patent 258,608 with German priority of October 12, 1925, protects for the I. G. Farbenindustrie A.-G. a process for the production of aromatic hydrocarbons especially of the benzene series which consists in passing methane or gas containing methane over a catalyzer under a high pressure of 50 to 300 or even 1000 atmospheres at temperatures between 500° and 800°.

The English patent 264,827 with German priority of January 19, 1926, protects for the I. G. Farbenindustrie A.-G. a process for the production of unsaturated hydrocarbons. According to the patent claims the process consists in this, that saturated aliphatic hydrocarbons such as methane or mixtures that contain it, are conducted over a catalyzer at ordinary pressure or at high pressure, at a temperature of 700° to 1000° or still higher with sufficient velocity to prevent a further condensation of the primary products into higher molecular hydrocarbons.

Finally, let me mention the French patent 610,543 of the "Société Anonyme, Le Pétrole Synthétique" of February 3, 1926, in which a process is described that is to consist of the transformation of methane into gaseous ethylene hydrocarbons or others that are still richer in carbon, and which is carried out in the following way. Methane is to be heated gradually and uniformly up to 750°<sup>16</sup> in

<sup>16</sup> In the corresponding English patent 261,267 of April 29, 1926, 950° is given.

layers as thin as 1 mm. This layer with a circular cross section is to be formed by the intervening space between two telescoping tubes, and the resulting gas is to be drawn off, while in the apparatus a low pressure of about a 20 cm. mercury column is maintained. The gases that have been heated are to be cooled suddenly and completely to the ordinary room temperature.

If one examines the different patents here, it is seen that liquid hydrocarbons are ordinarily produced under pressure and with the use of catalyzers. For the production of ethylene from methane, the use of high pressure is not demanded in the two last-mentioned patents. It is remarkable that the majority of patents working under pressure mention the production of petroleum hydrocarbons. Only in the patent of the I. G. Farbenindustrie A.-G. is it mentioned that benzene hydrocarbons arise, which corresponds with our results obtained at ordinary pressure. In none of the patents, however, is there to be found a clear assertion concerning the yields obtained. Only in the French patent 610,543 is there an observation that 80 per cent of the methane could be converted into ethylene and ethylene hydrocarbons. But we cannot tell from this remark whether all the methane is meant, or only that which has disappeared during the process. The latter would not give much information.

According to the patents cited whose claims have so far not been supported by other authorities, we might be led to believe, that for the production of benzene hydrocarbons in larger yields than are known at present in scientific literature, the use of pressure and of catalyzers is necessary. As a matter of fact, however, neither of them is necessary, and it is not yet known whether under the more detailed conditions of the patents cited better yields are attained, than can be attained with ordinary pressure in a single process.

The results at hand are only a beginning. But the fact that they could be attained in so simple a way, shows again that not even the elementary fields of chemistry have been thoroughly and completely studied.

#### SUMMARY

1. It was shown that methane can be converted into benzene and other benzene hydrocarbons, if it is heated to temperatures of 1000° to 1200°, when keeping the period of heating, however, shorter than 10 seconds. Under these conditions, processes can be carried out under ordinary pressure; catalyzers are not necessary.

2. Conditions can be so adjusted that the chief reaction product consists of benzene hydrocarbons, more than half of which is benzene. The amount of the unsaturated hydrocarbons in the residual gas can be reduced to 4 per cent, and the separation of carbon can be almost completely prevented.

## LOW TEMPERATURE PHANTOM

*By F. C. GREENE*

*Consulting Engineer, the Old Ben Coal Corporation, Chicago*

Permit me to define phantom as a mental image of a real object. Perhaps you agree that failure to "chase our favorite phantom" would result in a too familiar world. This spirit of coal intrigues the investigator. No sooner does he materialize it with a work-a-day body than he observes and pursues yet other phenomena.

Your speaker went home from the First Conference to rake up the leaves on his lawn; then to burn them beneath the bare boughs of an old maple. His small feathered friends had left their gaily painted home swinging by a stovepipe wire. Wrens are sensitive to odors. Their painted house was taken down. The stovepipe wire suggested a stovepipe, which was hung—in lighter mood, let us say—to see what would happen. After some manipulation the small chimney "draws" and smokes famously. The pipe becomes red and the smoke ceases. That is an odd fact. The pile of leaves is now huddled around the pipe until it hangs in a deep well of clear combustion. But only partial combustion under the down-draft, for occasionally gas could be ignited at the top of the pipe. I roughly sketch the simple apparatus (see fig. 1).

Its performance was quite erratic; but characteristic of those phantom forms that J. B. S. Haldane mentions as frequenting the borders of practice: mental images of real objects.

Turning tinsmith, during the long winter, your speaker endeavored to catch this phantom and put it at work in a variety of forms. Eventually the apparatus, now sketched, evolved (see fig. 2).

Coal screenings enter the rotating pan *A*, to which is attached a hollow screw *B*. The coal enters openings *C* in a stationary cylinder *D* and is elevated to the brim of *B* and fills it. Air enters at *E* and rubs a fire-wall *F* back of which is an important plastic coal layer *G*. Gas is made thereby and, passing up the red-hot tube *H*, burns at its top where, of course, it meets its full quota of air.

A great institution invited a demonstration of this immature apparatus (see fig. 4).

Its staff suggested your speaker apply the principle to apparatus to gasify thirty tons of coal per hour. Some study indicated it best

to turn the original device insides-out and effect the gasification upon the surface of a conical pile of coal that would grow as fast as it was consumed.

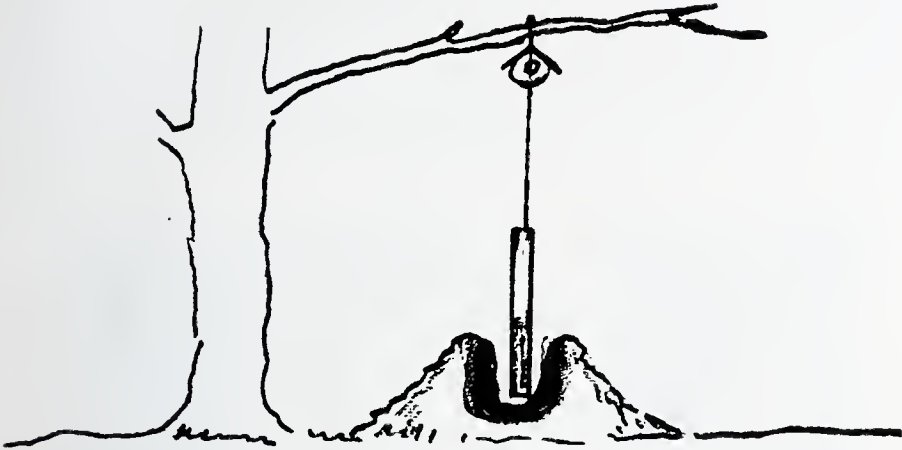


FIG. 1

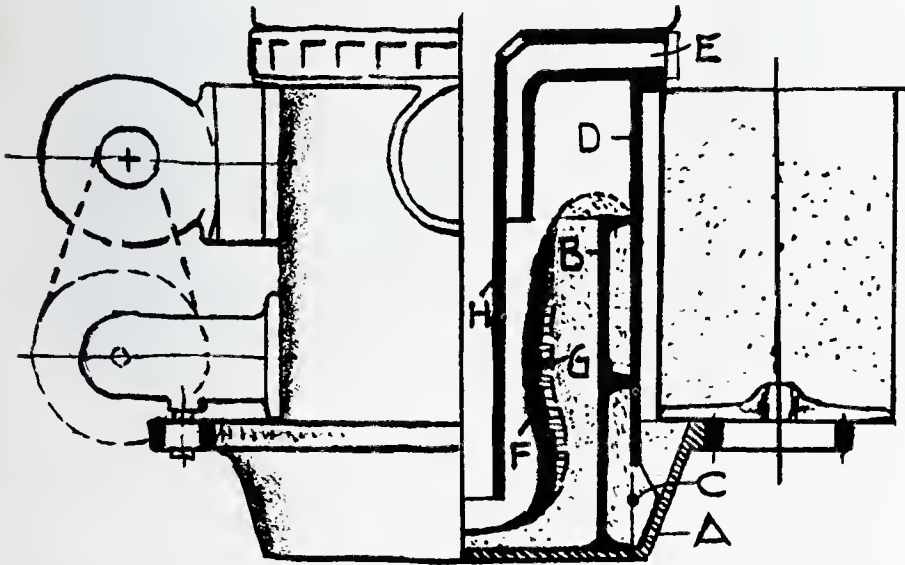


FIG. 2

The apparatus now took the form sketched below and will be developed along such lines by increasing size models (see fig. 3).

Referring to the three-letter symbols of this sketch you will be able to follow the flow thus: The screenings enter at hopper *HPR* and drop onto a stationary feed-screw *FDS* being propelled into the ap-

paratus by the rotation of the enshrouding feed-pipe *FDP* which is also the drive-shaft and upon the far end of which is the necessary bevel pinion meshing with like gear of the conical rotor *RTR* which rests upon rollers *RLR*. By an arrangement of portals and shutters at the base of the rotor the coal is admitted to the rotor flights *FLT* and by them elevated upward. At the hearth line the flights propel against an evasé boundary and the coal is then both propelled up-

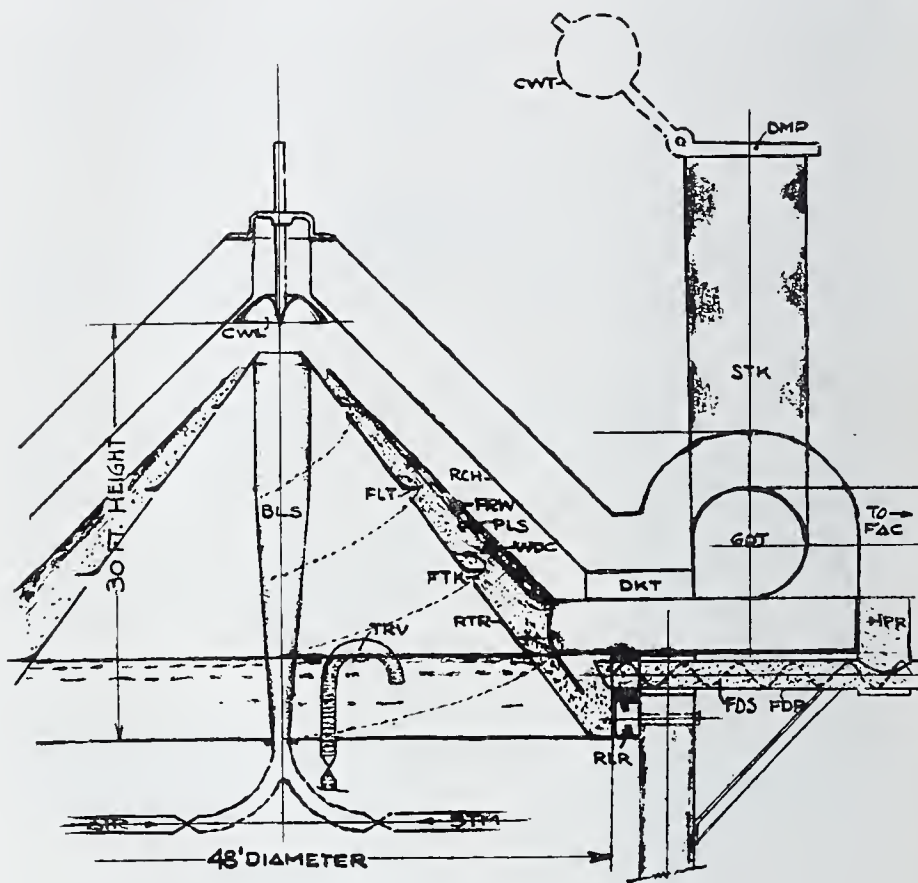


FIG. 3

wardly and outwardly. This dual propulsion continues to the top of the conical screw or rotor. In this manner is formed a hollow cone of coal which, ignited at its top will burn downwardly and form externally a fire-wall *FRW* beneath which will be a plastic layer *PLS* underlain by mixtures of wet and dry coal *WDC*. Beneath the rotor flights *FLT* are openings for the offtake *FTK* of the water and tar vapors educted to the interior of the rotor cone which is thus in a

manner a hydraulic main drained by a water and tar-vent *TRV* to a given level.

Air and steam inlets in the base of the apparatus function in the usual manner required for making air-gas, producer-gas or blue-gas. Assuming we are making air-gas then the air blast through the riser *BLS* impinges the reversing cowl *CWL* and travels down the fire-wall *FRW* which is encased within the conical arch *RCH*.

Several assumptions may explain what happens in the region between the fire-wall and the arch. I desire to afford you the pleasure

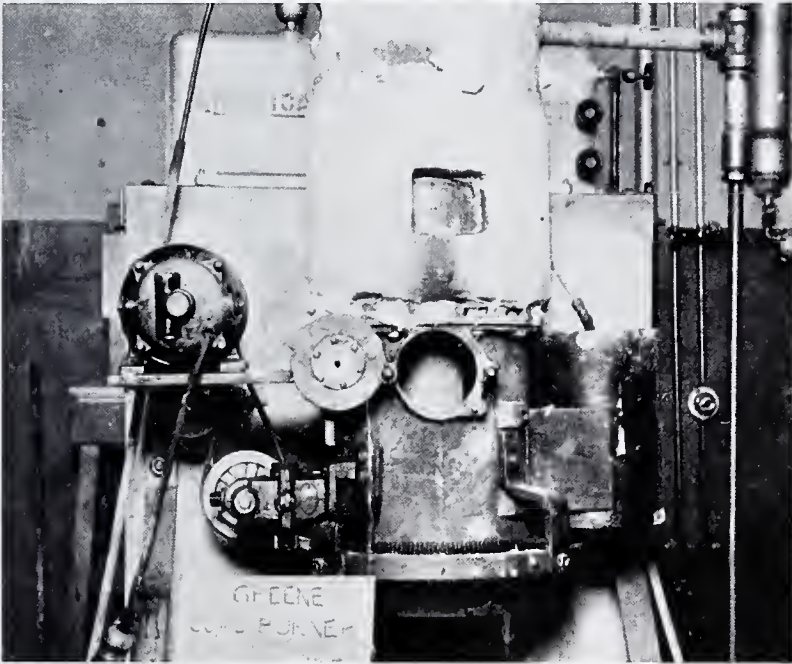


FIG. 4

of making what seems to you the correct solution. It may add to your pleasure to know that at the bottom of the heap the fire-wall is always deeply eroded. From experimental work we have determined some temperatures within the apparatus. The entering coal, say 80°F. The under surface of the plastic, 600°F. The upper surface of the plastic, 1,000°F. The fire-wall surface (whilst making air-gas), 3,000° to 3,500°F. The arch opposite such fire-wall points, 2,000°F. The gas-make, 1,500°F. These values are in round figures, of course, and result without preheated primary air. Again referring to the sketch, the air-gas leaves the apparatus through a series of

ducts *DKT* to enter a gas-offtake tunnel surrounding the generator. This torus-shaped offtake *GOT* will be provided with a stack *STK* dampered *DMP* in the usual manner with a counterweight *CWT* attached. A further outlet for the make-gas will lead to the fly-ash catcher *FAC* (of what sort, unknown to date).

The sketch shows the dimensions required for a generator gassing 1,000 pounds of screenings per minute. The model will be one-twelfth this size with capacity for gassing about 10 pounds of screenings per minute which should afford us much information.

I wish to call your attention to some of the characteristics of this low temperature phantom. First, it seems to indicate that generation of a low thermal value gas does not require blasting the air *through* a fuel bed. Second, since the blast removes the ash particles as fast as erosion releases them, they fly off in the gas stream and no ash remains in the apparatus. Obviously, there is no clinker. The nascent carbon surface is always clean. Third, very low blast pressure and velocities. Fourth, the gas is made on a low temperature char surface. No high temperature coke has been found. According to Fieldner and his coworkers, low temperature char converts  $\text{CO}_2$  to  $2\text{CO}$  about twelve times as fast as does hard coke. Clement and Woods classic speeds of reaction seem to be attained in this apparatus. Fifth, it is thought that the radiants from the fire-wall are much in excess of the requirements for making air-gas. We have considered their highly efficient employment therefor should steam generation pipes be placed suitably within the arch in manner as for the modern water-wall boiler.

This phantom has some dubious characteristics. First, its volcanic-like effluvia—its fly-ash—is, at present, not an unmixed blessing. Can it be slagged, precipitated, consolidated, so it will not fly? We are working on the problem. Second, can a higher thermal value gas be made by it? We are approaching that question with interest. Considering the fire-wall as being deeply fissured and the nascent clean carbon area, and hence weight, being favorable factors, one might think the blow period shortened and the run lengthened in making water-gas. During the run it would seem that far less fly-ash would be released. Third, will refractories stand up under the temperatures of air-gas making? We think the evidence to date so indicates. But, when it is attempted to slag the fly-ash within a refractory-lined furnace it becomes a problem of neutral refractory quality.

Some future possibilities are suggested by such apparatus: First, it would be, perhaps, worth while in making power fuel-gas to attempt recovery of the lighter tar-oils as a credit against coal cost. Such partial recovery may be expected from the subsurface of the plastic layer. Your speaker would expect almost no gas yield therefrom and about half the usual low temperature yield, but of a very light-oil quality.

Second, if our superpower stations are to seek for further credits to reduce off-peak losses, why not their latent energy be turned to account and made to effect other, and more important, conversions of the three raw materials—coal, water and air—entering into energy manufacture? Possibly that may be yet another low temperature phantom.

# SOME PHASES OF THE ORGANIC SULFUR PROBLEM IN THE MANUFACTURE AND UTILIZATION OF GAS

By WILBERT J. HUFF

*Professor of Gas Engineering, Johns Hopkins University*

The rapid development of modern industry through the agency of applied science has led to a phenomenal growth in the use of city gas for industrial purposes. Conveniently available, readily controlled, and capable of high efficiencies in the conversion of the potential thermal value of the raw gas-making material into useful furnace heat, city gas for industrial purposes has won its way on merit against most formidable economic and technical competition with other fuels.

In this competition manufactured gas possesses an advantage which is not generally stressed, namely, in the low content of sulfur contained in the products of combustion. Thus it is not unusual for a low sulfur coal and oil to give from thirty to fifty times the sulfur per British thermal unit that is given off by the combustion of an equivalent amount of city gas. This low sulfur content is due to the removal of hydrogen sulfide, which is easily accomplished with the iron oxide, or one of the liquid purification processes of gas making. It is needless to speculate here upon the economic and humanitarian value of the great reduction in the sulfur which accompanies the increasing preference for manufactured gas for industrial and central househeating purposes. These important considerations have been touched upon by others, notably Dr. S. W. Parr in his Presidential address before the American Chemical Society in St. Louis this year.<sup>1</sup>

Sulfur in burning fuels gives sulfurous and sulfuric acid which attack appliances and accessories.<sup>2</sup> The corrosion of boiler and heating plants, metallic recuperators and metallic and refractory flue parts can be attributed to the action of these acids. In many operations the high content of sulfur in the combustion products prevents the direct application of these to the furnace charges. The user of

<sup>1</sup> *Ind. Eng. Chem.*, 20, 454 (1928).

<sup>2</sup> Christie, A. G.: *Power*, 65, 87-8 (1927).

Donath, *Brennstoff Chem.*, 2, 26-8 (1921).

manufactured gas therefore enjoys important direct advantages over the user of other competing fuels.

The small quantity of sulfur present in manufactured gas is that in the form of gaseous organic sulfur compounds which are not removed in the ordinary purification processes.

In many of the proposed catalytic syntheses for the production of alcohols, or motor fuel hydrocarbons from water gas, or of ammonia from the hydrogen of gas making processes, the organic sulfur compounds serve as a poison which seriously diminishes, and may completely destroy the activity of the catalyst. This is also true of catalytic enrichment processes, such as proposed methanation processes.

While these last named processes are not at present of value to the general gas and fuel industries of America, certain of them are of considerable importance from a chemical standpoint; and the successful solution of the organic sulfur problem at a minimum of expense, an end towards which the development of these processes is undoubtedly contributing, is a desideratum of unquestioned importance to the gas and fuel industries.

Recent published researches have shown that the organic sulfur compounds enter into other reactions of interest. While the gas is being handled in works equipment, holders, mains, services and meters, a slow decomposition may occur to form very deliquescent corrosive sulfur salts which, through the corrosion which they stimulate and the attendant deterioration of meter diaphragms which they may cause, are a primary source of some of the most important depreciation of the capital investment of a gas company.<sup>3</sup>

Further justification for research upon the organic sulfur is hardly required, but may readily be found in such topics as the use of high sulfur coals and gas oils whose extensive employment in this country is now restricted because high concentrations of organic sulfur are prohibited under the public utility regulations of the various states.

The organic sulfur problem in its various phases is therefore a matter of some concern to those who are interested in the technical development of manufactured gas. For this reason, it is one of the problems before the Department of Gas Engineering at Johns Hopkins, and the Department has been and is now engaged in laboratory

<sup>3</sup> Taplay, *Gas World*, 70, 451 (1919), *Gas J.*, 146, 622 (1919); *Gas World*, 72, 481 (1920), *Gas J.*, 150, 583 (1920).

studies of certain of its phases. Since these are probably less familiar to the members of this conference than are other more important studies elsewhere, this paper will deal in a large part, though not exclusively, with the subject matter of some of these researches.

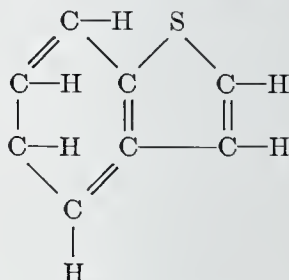
#### THE CONSTITUTION OF THE ORGANIC SULFUR COMPOUNDS IN GAS

Other than the fact that carbon disulfide usually contributes the most of the organic sulfur found in gas, very little is known of the constitution and occurrence of the various organic sulfur compounds which may be present. This was voted one of the most important problems before the 1927 Chemical Committee of the American Gas Association and the university has offered to coöperate with the Association in pursuing the necessary experimental work.

The following compounds have been identified in tar oils, and may therefore be found in commercial gases under some conditions.

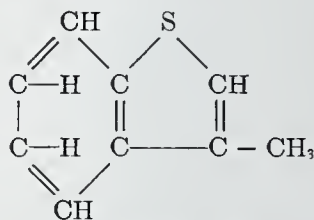
$\text{CS}_2$   
Carbon disulfide<sup>4</sup>

$\text{R}-\text{S}-\text{H}$   
Mercaptans in which the  
R may represent an alkyl  
or an aryl group.<sup>5,7</sup>



Thionaphthene<sup>6</sup>

$\text{R}-\text{S}-\text{R}$   
Sulfides, in which the R may  
represent an alkyl group.<sup>7</sup>



Thionaphthene 2-methyl<sup>8</sup>

<sup>4</sup> According to Hutton and Thomas, *Gas Age*, 47, 88 (1921), carbon disulfide may represent as much as 80 per cent of the total sulfur in manufactured gas.

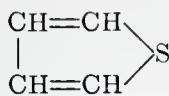
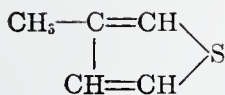
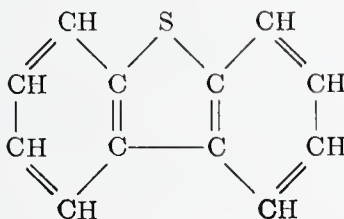
<sup>6</sup> Schutz, Buschman and Wissebach: *Ber.*, 56, 1967 (1923).

<sup>7</sup> J. Boes: *Apothekers Zeit.*, 17, 565 (1902).

Weissgerber and Kruber: *Ber.*, 53B, 1566 (1920).

<sup>7</sup> F. Schutz: *Ber.*, 56, 162 (1923).

<sup>8</sup> Weissgerber: *Brennstoff Chem.*, 2, 1 (1921).

Thiophene<sup>9</sup>Methyl thiophene<sup>10</sup>Diphenylene sulfide<sup>11</sup>

The thiophene and methyl thiophene are found with benzene and toluene. The thionaphthene and thionaphthene 2-methyl are found with naphthalene and the methyl naphthalenes, while the diphenylene sulfide is found in the anthracene fraction. The other compounds occur chiefly in the forerunnings and light oils.

The determination of the constitution of such compounds as may occur, and the correlation of the gas manufacturing conditions with variations in the composition and amount of these organic sulfur compounds are an important phase of the whole problem. In fixing the constitution, the prediction of chemical processes which may be available for the decomposition and removal is very much simplified.

The determination of the causes of the variation in the respective compounds offers the interesting possibility that comparatively simple changes in the technique of gas manufacture may greatly reduce, if not completely prevent, the formation of these undesirable materials. If this can be done economically this will, of course, be the ideal solution of the organic sulfur problem.

A preliminary study along these lines has been already published as a result of our work at Johns Hopkins. This work has dealt chiefly

<sup>9</sup> V. Meyer: *Ber.*, 16, 1465 (1883).

Frankel: *Arzneimittels Synthesen*, 3rd Ed., 1912, 681.

<sup>10</sup> Meyer and Kreis: *Ber.*, 16, 1624, 2970 (1883).

Pfaff and Kreutzer: *Z. angew. Chem.*, 36, 437 (1923).

K. E. Schulze: *Ber.*, 18, 3852 (1885).

Pfaff and Brunck, Private communication, to Furth and Jaenicke, *Z. angew. Chem.*, 38, 170 (1925).

<sup>11</sup> Boes: *Apothekers Zeitung*, 17, 638 (1902).

Kraemer and Weissgerber: *Ber.*, 34, 1662 (1901).

with carbon disulfide which furnishes the major portion of the organic sulfur impurities. Before it could be pursued, however, it was necessary to simplify certain analytical procedures.

#### ANALYTICAL PROBLEMS

At the time the study was begun, no satisfactory method for the convenient detection of small quantities of carbon disulfide in gas was available and it was necessary to develop such a procedure. The reaction of carbon disulfide to form xanthate was taken as a basis for one method and a study of the factors affecting the precipitation of small amounts of cupric xanthate was made.<sup>12</sup>

This study emphasized the importance of fixing within rather close limits the concentration of the various reagents and suggested the possibility that some of the criticism directed against the potassium xanthate methods for carbon disulfide lay in the failure to appreciate this necessity. Since the development of these conditions, an excellent colorimetric method for carbon disulfide using the xanthate reaction has been published by G. G. Désy of the Koppers Company laboratory.<sup>13</sup>

While these methods have aided the attack upon certain phases of the organic sulfur problem, they do possess the disadvantage that they deal only with carbon disulfide and there is a need for a simple method which could be used for total organic sulfur. Taylor, in his book on Industrial Hydrogen<sup>14</sup> has pointed out that certain catalysts which decompose carbon disulfide to form hydrogen sulfide furnish a convenient means for detecting small amounts of organic sulfur. The catalysts which he mentions are platinized pumice or reduced nickel at a temperature of 500°C.

This qualitative method suggested a convenient procedure for the rapid quantitative determination of organic sulfur, and this has been developed by Dr. Oscar W. Lusby<sup>15</sup> in the laboratory of the writer. So far it has only been adapted for use in the determination of organic sulfur in blue gas but Mr. John C. Holtz, working at Johns Hopkins, has found the method satisfactory for certain carburetted gases. Because of the convenience of the method and because it has not hitherto been published, a discussion of its essential features will be given.

<sup>12</sup> *Jour. Am. Chem. Soc.*, 48, 81 (1926).

<sup>13</sup> *Proc. Am. Gas Assoc.*, 1927, 1440.

<sup>14</sup> H. S. Taylor, *Industrial Hydrogen*, 199, Chemical Catalog Co., (1921).

<sup>15</sup> Research Associate in Gas Engineering at Johns Hopkins University.

Many of the catalysts tried, such as silver, chromium, promoted iron, and platinized asbestos, were found unsatisfactory for the quantitative determination because they held back large amounts of sulfur, probably as the sulfide or intimately mixed with carbon deposited on the catalyst. Considerable time was therefore required before the concentration of hydrogen sulfide in the outgoing gas stream corresponded with the sulfur in the entering gas. Accordingly, Dr. Lusby tried a new and different procedure. This method depends essentially on the use of a platinum spiral heated electrically. This catalyst has the advantage that it holds back little if any of the sulfur. The apparatus consists of a pyrex tube about 14 inches long and  $1\frac{1}{8}$  inch in diameter in which is suspended a platinum coil heated to bright red, almost white, heat by an electric current. The coil is approximately 8 inches long and  $\frac{1}{2}$  inch in diameter and is made from 5 feet of No. 30 B. & S. gauge wire. The coil is suspended on a vitreosil rod  $\frac{1}{8}$  inch in diameter and is electrically connected by heavy copper leads passing through rubber stoppers at each end of a glass tube. Organic sulfur in the gas, on passing through this coil, is converted to hydrogen sulfide which may be determined in the effluent gases by means of a Tutwiler burette and standard iodine solution. Since the amounts of hydrogen sulfide present are normally very small it has been found convenient to use burettes in the form of the ordinary Tutwiler of gas works practice with the exception that they are arranged to take 500 cc. samples instead of the usual 100 cc. It is also desirable to have iodine solutions of such a strength that one cubic centimeter equals one grain of sulfur per 100 cubic feet of gas. The following are some of the results obtained by Dr. Lusby and Mr. D. T. Bonney<sup>16</sup>

	VELOCITY OF GAS THROUGH COIL, CUBIC FEET PER MINUTE		
	0.01	0.05	0.1
	Grams of sulfur per 100 cubic feet converted to hydrogen sulfide by spiral		
At start of test.....	5.15	5.4	5.0
After $\frac{1}{2}$ hour.....	5.6	5.7	5.1
After 1 hour.....	5.8	5.6	5.2
After $1\frac{1}{2}$ hours.....	5.7	5.6	5.0
Average (omitting first determination).....	5.7	5.62	5.1

<sup>16</sup> Research Assistant in Gas Engineering at Johns Hopkins University.

The experiments were made on blue gas which was analyzed according to the usual Referee procedure.<sup>17</sup>

These results showed that at the low space velocities the method is satisfactory for the determination of the total sulfur in blue gas. At the higher space velocities it appears that a small portion of the sulfur passes through without being converted to hydrogen sulfide. The method immediately after the start of the test gives results which are rather too low. This is probably due to the tendency of the platinum wire to absorb sulfur as was noticed by Taylor and Pickett.<sup>18</sup>

After the spiral had been used for about two months further tests were made to determine its accuracy. The following results were obtained with blue water gas found to contain 8.3 grains of sulfur per 100 cubic feet, using the Referee method.

Velocity of gas through spiral, 0.03 cubic foot per minute

Time between determinations, hours.....	At start of test	1½	¼	1	¾	1	Average omitting first deter- mination
Grams of sulfur per 100 cubic feet converted to hydrogen sulfide.....	7.4	8.5	8.3	8.5	8.6	8.4	8.46 obs.

Further tests with fresh iodine solution

Time between determinations, hours.....	½ hour after start of test	1	1	1	Average
Grams of sulfur per 100 cubic feet converted to hydrogen sulfide.....	8.4	8.3	8.6	8.6	8.47 obs.

These results when corrected for the temperature and pressure averaged 8.7 grains per 100 cubic feet. While this is somewhat higher than the Referee method, the convenience of the platinum spiral method is so great that it outweighs small differences in the accuracy of the determination.

It is expected that this method or some modification of it will furnish a convenient means for estimating the organic sulfur in

<sup>17</sup> *Gas Chemists Handbook*, pages 339-42. (2nd Ed.)

<sup>18</sup> *J. Phys. Chem.*, 31, 1212 (1927).

manufactured gas. The chief disadvantage in its application appears to lie in the possibility of tar formation or carbon deposition due to the decomposition of the illuminants. Mr. John C. Holtz, at the suggestion of the writer, has examined certain of these tar and carbon deposits but has so far not found the retention of important amounts of sulfur. The matter should, however, be pursued further.

#### THE ORIGIN OF CARBON DISULFIDE IN THE CARBONIZATION OF COAL

The initial experimental work on the origin of carbon disulfide dealt with the formation of this compound in a small coal carbonization test.<sup>19</sup> Previous investigators had noted that under laboratory conditions carbon disulfide did not appear in the gas and this was ascribed to the small time of contact between the sulfur-containing gases and the carbon surfaces. The investigations at Johns Hopkins showed that the essential phenomena in this formation or non-formation of carbon disulfide was associated with the rapid change in the temperature of the coal undergoing the carbonization. Coal whose temperature was changed very rapidly gave large quantities of carbon disulfide while coal whose temperature was changed slowly gave no detectable amounts of carbon disulfide. This study also showed that heated coke surfaces under certain conditions decomposed the carbon disulfide contained in a raw gas stream instead of forming this compound by reacting with hydrogen sulfide. This observation was apparently in contradiction with the generally accepted theory for the formation of carbon disulfide. It was suggested that this behavior could be explained by assuming that the sulfur was distributed heterogeneously and that sudden heating caused the local formation of carbon sulfur complexes high in sulfur while slow heating permitted the sulfur to pass out as hydrogen sulfide or to remain behind in non-volatile association with the coke.

#### THE FORMATION OF CARBON DISULFIDE IN THE CRACKING OF OIL —THE CARBON SULFUR COMPLEX

This matter was further studied by the writer in collaboration with Mr. John C. Holtz,<sup>20</sup> using as a homogeneous gas making material, a high sulfur gas oil. Here again heterogeneous conditions developed during cracking due to the formation of so-called retort

<sup>19</sup> *Ind. and Eng. Chem.*, 18, 357 (1926).

<sup>20</sup> *Ind. and Eng. Chem.*, 19, 1268 (1927).

carbon. To determine the part played by this and by the hydrogen sulfide a number of experiments were made using medicinal oil and hydrogen sulfide and also sugar charcoal and hydrogen sulfide. A large amount of hydrogen sulfide was decomposed in the cracking experiments without producing a corresponding amount of carbon disulfide, and when sugar chars were used an extended delay was noted before carbon disulfide was produced in sufficient quantities to be detected. This delay appeared to be increased with an increase in the heated carbon surfaces. This phenomenon can best be explained by the assumption of the formation of carbon sulfur complexes which, when sufficiently high in sulfur, decompose to give carbon disulfide. It is therefore believed that such complexes play a very important part in the formation of much of the organic sulfur in gas.

If it is granted that these complexes are synthesizing points for the production of carbon disulfide, the interesting possibility of suppressing the formation of the carbon disulfide by preventing the formation or decomposition of these complexes is presented. Thus, it may be possible to deposit a catalyst upon the carbon surface to favor the elimination of the sulfur as hydrogen sulfide or the elimination of the carbon through the gasifying action of steam, oxygen or hydrogen. This matter is now under inquiry at Johns Hopkins University by Mr. John C. Holtz. This investigator finds that the addition of small quantities of a certain metal to an oil undergoing cracking causes a decrease in the sulfur in the gas, both the hydrogen sulfide and the organic sulfur being decreased, the decrease in organic sulfur being relatively the greater. The reduction in sulfur in one case was 177 per cent of that which would be expected if the sulfur were retained only as the metallic sulfide. This result is, of course, only preliminary, and the matter will be investigated further.

#### ELIMINATION OF ORGANIC SULFUR FROM GAS WHICH HAS BEEN COOLED AND DETARRED

The foregoing lines of attack upon the organic sulfur problem may not appear to offer the possibilities for elimination of organic sulfur comparable with those which are offered by other processes which may be used on the cold, detarred gases, as for instance, in certain catalytic methods. An examination of the economics of these will show, however, that no matter how attractive such processes may appear to industries, such as the synthetic methanol and synthetic

ammonia industries, which can bear a high charge for the purification of gas, the charges are not permissible in the general American manufactured gas industry. Thus the cost of the raw fuel necessary to raise the temperature of the cold, detarred gas to  $500^{\circ}\text{C}.$ , as required by one recent catalytic process, may in itself exceed the present charge for the removal of hydrogen sulfide by the usual iron oxide process and this charge and other charges must be carried in addition to the usual hydrogen sulfide removal charges. On this ground alone it is believed that inquiries such as are detailed above may be justified.

### DISCUSSION

A. E. BLAKE (United Gas Improvement Company, Philadelphia, Pa.): I would like to ask a question, whose answer can only be guessed at, but the opinion of the speaker might be of value; namely, what is it worth in cents per thousand to be completely rid of organic sulphur in addition to complete removal of hydrogen sulphide?

DR. HUFF: As Mr. Blake says, at present we can only speculate. No one has made, to my knowledge, a careful study of the economics involved to determine what charge would be justified for the removal of this organic sulphur.

DR. GUSTAV EGLOFF (Director of Research, Universal Oil Products Company, Chicago, Ill.): I am not certain that I understood Dr. Huff correctly, in the early part of his address, when he stated that sulphur in gas corroded or pitted the steam boiler furnace, and so on.

I hope I am mistaken, for the reason that the oil industry burns probably billions of cubic feet of natural gas and petroleum gas daily which contains as an average probably one per cent of hydrogen sulphide and some of it as high as 12 per cent of hydrogen sulphide, and never has it discovered corrosion in any part of its furnaces or its steel heating surfaces.

Likewise the fuel oils that are burned throughout the United States and the world run from a half per cent sulphur content by weight to over 6 per cent sulphur by weight. Exhaustive tests have been made, and no one has been able to discover signs of corrosion of any material at all.

Did I understand you correctly?

DR. HUFF: Mr. Chairman, I repeat the assertion that sulphur is objectionable. I think, however, that it should be qualified. This corrosion occurs chiefly where the flue gases are cooled to their dew point rather than upon high temperature surfaces.

I am astonished at the statement that sulphur in combustion does not cause corrosion, because that is the first time I ever heard it made. I am surprised that the question has come up at all. But I do, however, take the blame for the fact that I should have explained it more thoroughly,

DR. EGLOFF: There is nothing astonishing about it, because we use concrete stacks and cement-line our furnaces, and the lowest temperature is 400°F. We do not get condensation of our water and hence we do not get corrosion in our system.

Surely Dr. Huff does not recommend categorically that we desulphurize all our fuels to preserve some particular metallic part in an industry that he is familiar with. If you wish, we simply put in proper alloys that will not corrode, even though the moisture condenses and the sulphur trioxide, produces sulphuric acid. It is staggeringly expensive to desulphurize gas and fuel oils, and in many cases utterly uneconomic.

MR. BLAKE: We had a little experience in the consideration of some of these alloys, and we know that the people working for high-efficiency house-heating furnaces have been driven to the use of some of these, that cost perhaps 50 cents a pound, and the householders do not like to bear the expense.

CHARLES TURNER (Glasgow, Scotland): I would like to ask Dr. Huff if he agrees with me that when heating water for the conversion of steam, using fuels with high sulphur content, condensation takes place in the surface of the plate and corrosion results, and when generating steam with high pressure, 300 or 400 pounds per square inch, still burning efficiently, the temperature of the gas is too high for condensation and no corrosion takes place.

DR. HUFF: I think I would agree with that statement in general, that the temperature conditions and humidity conditions have a great deal to do with this corrosion.

The fact is, that where you are attempting to use your fuel efficiently and do run your flue gases down to a very low temperature, so low a temperature that condensation of moisture may be expected, I believe it is safe to say that you may expect some sulphur corrosion from any fuel.

But I believe it may be said that in the case of many oil burners, the efficiency may not be carried to this point and, moreover, there may be a protective oil film deposited, due to incomplete combustion of the oil and tar. In such cases corrosion may not be so serious. But certainly poor combustion is not a condition to be proud of. Tests which we have made at the University have shown that important loss in efficiency occurs in many oil burners due to the fact that the combustion is so poor that some partly burned hydrocarbons escape.

In the gas industry a combustion condition that would allow as much as 10 per cent of the heat value to go up the stack in partially burned products would not be considered satisfactory and therein lies a difference in the burning of some gas and some oil.

DR. EGLOFF: This is just a statement of clarification. The usual charge and the very favorite one against the oil industry is its state of high inefficiency.

Now we have the leading combustion engineers of the world, inclusive of professors of universities, who are candid in trying to assist us in burning our

fuels with the greatest efficiency. And the changes in the last ten years have shown that they are coming somewhere near the ideals of efficiency.

But Dr. Huff forgets that in burning hundreds of billions cubic feet of natural gas and cracked gases and refinery gases, where they can be burned efficiently, the sulphur content averages something like one per cent of hydrogen sulphide, and we do not know the problem of corrosion in the oil industry from the standpoint of condensed water in the furnaces.

DR. HUFF: I do not want to carry this further, but it occurs to me that the Koppers Company built in Canada, not so long ago, a liquid purification plant for the purpose of removing hydrogen sulphide from natural gas, and one reason was because it was found that corrosion in the water heaters made this removal necessary. I think a great many other instances could be cited to show that sulphur in a fuel is objectionable.

A. KOSEL (People's Gas, Light & Coke Company, Chicago, Ill.): I do not understand Dr. Egloff's comment on Dr. Huff's research in the eliminating of sulphur. Half of the biggest part of our investment is in the equipment for the removal of sulphur, and we more than welcome any research in this direction to eliminate this equipment and naturally and economically be more sound than before.

I personally welcome any research or endeavor in the eliminating of sulphur, whereby we can eliminate these machines or this equipment and possess something better, or a resistant material against sulphur.

I just wonder what Mr. Egloff's idea is in resisting or being contrary to research in this direction.

MR. EGLOFF: You probably did not follow me. I have no quarrel with taking sulphur out of gases for domestic uses. I discussed the proposition of sulphur in combustion fuels, relating to industrial use in a furnace, in the oil industry, and that in the burning of the fuels that I mention we never ran up against the problem of corrosion.

I am quite familiar with the fact that you have to take it out of city gas. We sell some of our gases that contain one per cent sulphur to public utilities, and before they can use it, they have to desulphurize it and use the wet method or dry method to do that.

MR. BLAKE: There is one phase of sulphur corrosion commonly lost sight of, which it might be well to mention. Consider a steel stack with the customary film of iron oxide completely coating it; also sulphur dioxide (with traces of the trioxide present) in stack gas at temperatures which may be somewhat above the condensation point of water vapor. This presents the case of a condition for a very common class of chemical reaction; that is, reaction between basic anhydride (iron oxide) and acid anhydride (sulphur dioxide) to form a salt (in this case iron sulphite). This salt can exist at temperatures between, say 212°F., and some higher, dissociation temperature. A film of such a compound is harmless, no doubt, while dry, but during rain the somewhat soluble iron sulphite will be removed, and since it is acid in solution, by hydrolysis, we will have intermittent corrosion at least. Please note that Mr. Egloff specified that the stacks he has been talking about are of concrete, which would account for the lack of complaint, it would seem.

## PRODUCER GAS FOR FIRING BOILERS

*By* WILLIAM B. CHAPMAN

*Consulting Engineer, New York*

During the past three years the development of the mechanical gas producer has progressed to a point that justifies the serious consideration of producer gas as a possible fuel for boiler firing. Gaseous fuel can be burned more efficiently and controlled more readily than solid or liquid fuel. The best that can be said of any fuel is that it "burns like gas"—that it makes a good "imitation gas." And producer gas is the cheapest and most universally available of all combustible gases.

A gas producer firebed is like any ordinary firebed except that it is two to ten times thicker, and only about 40 per cent of the air for complete combustion is delivered under the grate, the balance being supplied at the point of final combustion. Most gas producers made today have mechanical agitation either at the bottom or top of the firebed—or both. The air blast beneath the firebed usually contains sufficient steam to enrich the gas to the desired point and to prevent clinkering. This amounts to from 20 to 40 per cent of the weight of the coal gasified. Hot producer gas as it leaves the producer usually possesses about 95 per cent of the energy of the producer input. The producer heat balance usually shows only 85 to 90 per cent efficiency for the hot gas, but it does not take into account the tar and oil vapors or the 2 per cent of fine carbon usually entrained with the gas.

Existing applications of producer gas to boiler firing may be divided into two groups, both of which, although successful, have a somewhat limited field of use. The first group is composed of detached installations in which the use of producer gas for boiler firing is incidental to its use for heating industrial furnaces, and only a minor portion of the gas is diverted to the boiler house. Such installations have been limited to sizes under 300 h.p. They are quite successful and usually save a third of the fuel formerly required and most of the labor. There are about a half dozen such installations in this country. From them we have been able to prove some of the merits of producer gas for boiler firing.

The detached type of installation of boiler and gas producer has

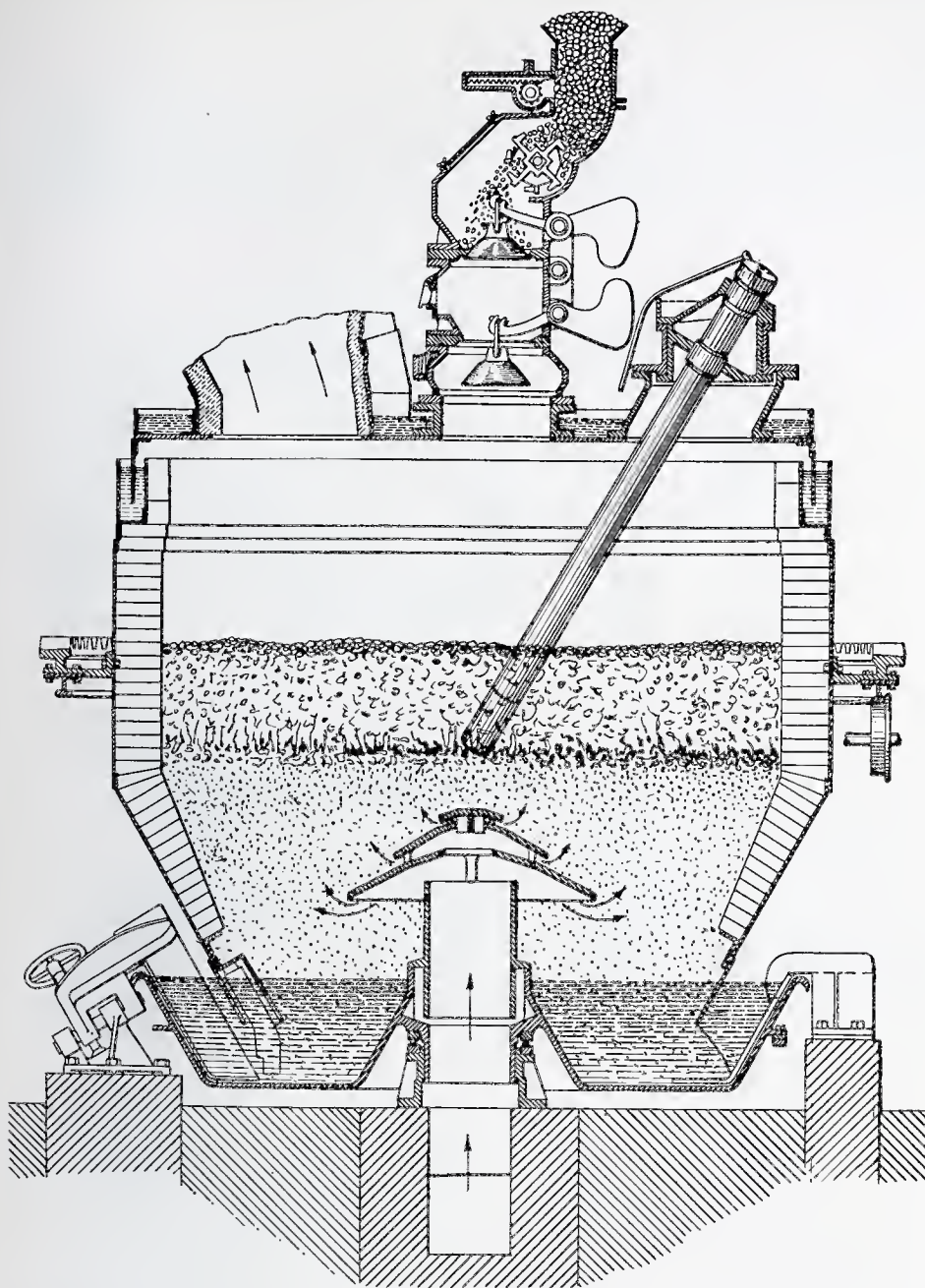


FIG. 1. WELLMAN-SEEVER-MORGAN PRODUCER

The chief feature of this producer is a semi-vertical stirring finger which reaches to within a few inches of the bottom of the firebed, if the ash level is maintained at the proper height. The stirring finger swings back and forth from the center to the wall while the producer walls and firebed, which they support, revolve normally at the rate of one revolution in ten minutes. The makers of this producer are the chief exponents of "Vertical Agitation." The ashes are removed by an adjustable plow in the revolving ash pan. There is no connection between the ash pan and the walls. The friction of the revolving firebed upon the ashes in the pan causes the pan (which has no driving mechanism) to revolve, the rate being regulated by an automatic locking and releasing device. This producer is a refinement of the Hughes, which was the first successful mechanical gas producer in the United States.

the advantage of being able to utilize any of the mechanical producers on the market, but is open to the objection that it occupies considerably more space and, due to larger radiation losses, is less

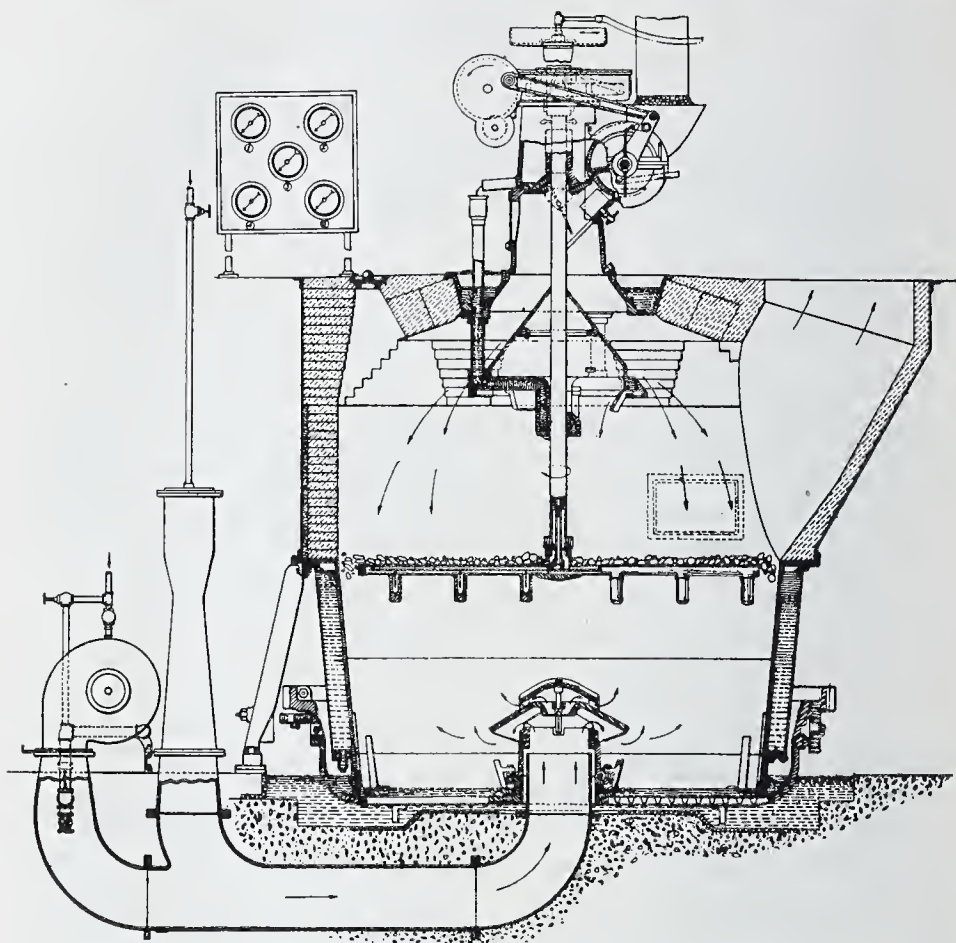


FIG. 2. CHAPMAN PRODUCER

This producer has separate agitating members for the top and bottom of the firebed, which operate horizontally. The top agitator automatically varies in height to agree with the top of the firebed, and normally revolves at seven revolutions per hour. The tuyere-hood and the beam in the ashbed, with its vertical fingers, revolve normally at one revolution in two hours. The makers of this producer are the chief exponents in the United States of "Horizontal Agitation." They also advocate cooled walls. The ashes are removed continuously by a series of revolving scoops set at different heights. The amount of agitation for the upper and lower portions of the firebed may be varied to suit the nature of the fuel and the rate of gasification. There are over two thousand of these horizontal agitating devices in operation.

efficient. It is also more expensive on account of the flues and valves and separate walls for the producers.

The second group is composed of integral combinations of small boilers and hand-operated gas producers. There are several such installations in England, combining the Wollaston stationary hand-

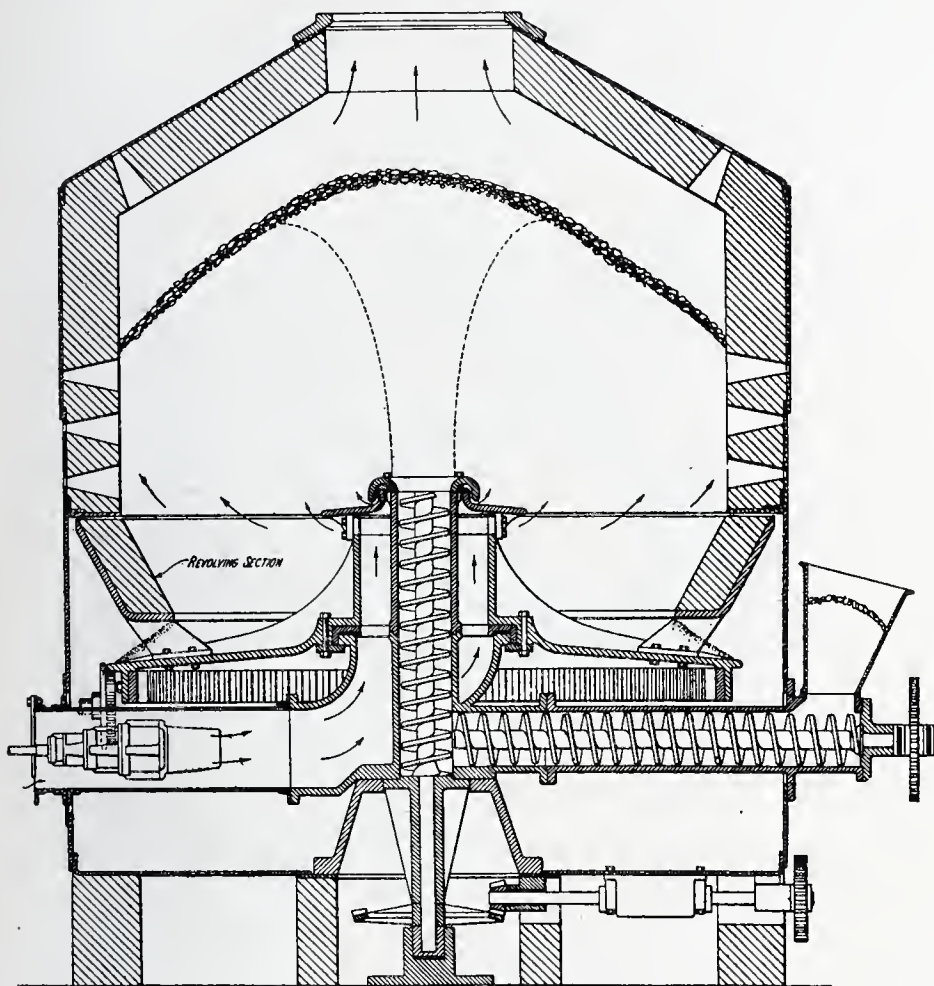


FIG. 3. GRAY UNDERFEED GAS PRODUCER FOR SLACK COAL

This producer was built and operated for several months in 1914 by the Ford Motor Company. Very gratifying results were obtained for a few days at a time but could not be maintained continuously, due partly to the clinkers adhering to the lower refractory walls and partly to the lack of a mechanical clinker-crushing and ash-removing device.

operated producer with the Cochran low-pressure boiler which is built around and over the producer. A beginning has also been made in Germany. This built-in type of gas producer and boiler is highly efficient and decidedly successful, but since the producer is

hand-operated, the size of each unit is limited to about 200 h.p. and since bituminous fuels are more difficult to handle, they are not used. Nevertheless, the efficiency of the Wollaston producer-boiler

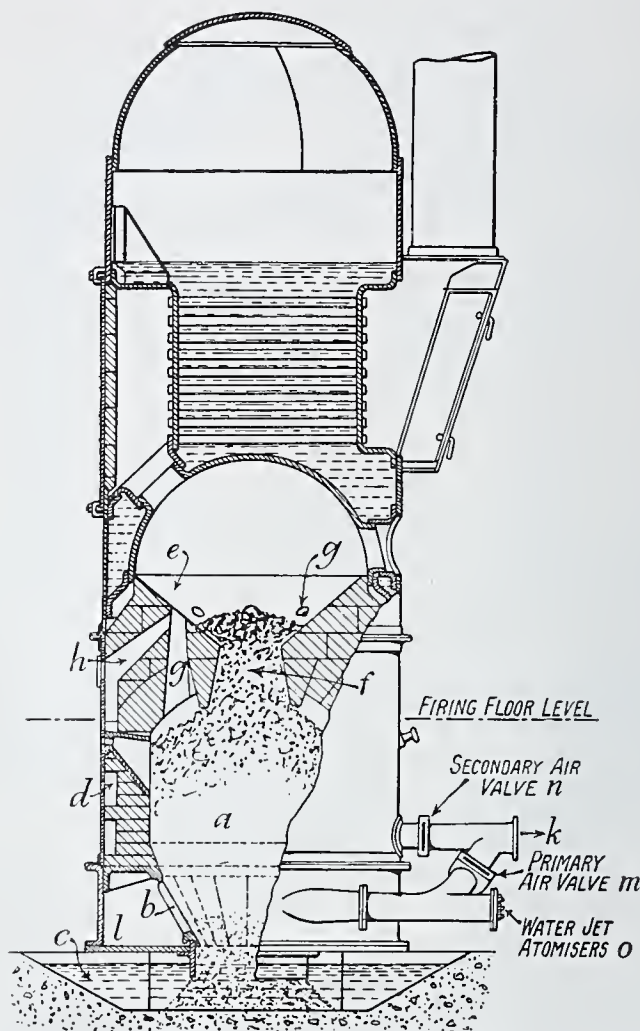


FIG. 4. WOLLASTON GAS PRODUCER COMBINED WITH COCHRAN BOILER

During the past two years several installations using coke breeze have been put into successful operation in England. About 40 per cent of the air required for complete combustion is delivered through the conical grate; the balance is preheated by passing spirally upward inside the shell and then discharged into the various streams of hot producer gas coming from the gathering chamber over the firebed. The efficiency is equal to the best obtainable in super-power plants.

is fully 90 per cent when using good coke and over 80 per cent when using wet coke breeze. The  $\text{CO}_2$  in the stack gases averages over

17 per cent. The recent coöperation of the British Government in the testing and developing of this new type of steam generator is bringing about important progress.

Another application of producer gas for boiler firing is for the auxiliary firing of waste-heat boilers in municipal gas works to augment their productive capacity. The Woodall-Duckham Company of England have an installation of this kind using coke in a hand-operated producer. Although the boiler is designed for waste

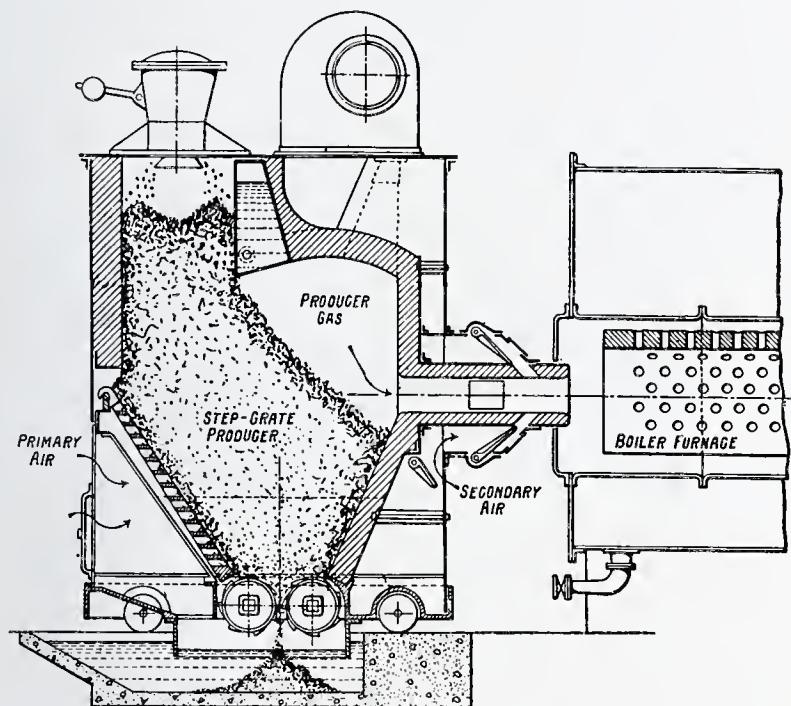


FIG. 5. DETACHED TYPE OF WOLLASTON PRODUCER CONNECTED TO A LANCASHIRE BOILER

The detached type does not give as good efficiency as the combined type and requires more floor space. It has, however, the advantage of not requiring a special type of producer.

heat and no economizer or air preheater is used, an overall efficiency of 86 per cent is maintained without difficulty.

The author believes that the integral combination of boiler and producer is the more promising. However, if large capacities are to be attained with the integral type, the hand-operated producer now used must be abandoned for a modern mechanical producer specially designed for this service. Such a producer would make possible the efficient use of all of our low-grade solid fuels; and the size of a single

unit could then be increased to 2,000 h.p. Furthermore, several 2,000 h.p. producer units might be grouped together under one large boiler and much larger capacities obtained.

The company with which the writer is connected has three conventional installations of mechanical gas producers which divert a minor portion of their output for the purpose of firing boilers. These installations use boilers varying from 100 to 150 h.p. No special boiler fireman is employed. The gas house boss performs the extra work of looking after the boilers as well as making the additional gas. The coal saved varies from 25 to 35 per cent of the amount formerly required.

The Commercial Testing and Engineering Company of Chicago made an elaborate 8-hour test of one of these installations having a 150 h.p. Geary Water Tube Boiler fired with gas from producers located some distance away. It showed that the combined net efficiency of the boiler and the distantly located producers was 76.1 per cent using Illinois coal. Formerly the CO<sub>2</sub> in the stack gases of the hand-fired boiler averaged 8.1 per cent. The change to producer gas increased the average CO<sub>2</sub> to 15 per cent. The saving in coal was 34 per cent. The report goes on to state that: "The remarkable increase in efficiency when burning producer gas can be attributed to the high efficiency of combustion made possible by the control of air admission at the gas burners and to the fact that no soot deposit was left on the tubes to interfere with heat transmission. The performance was smokeless at all times."

The coal as fired in the producer was 9.48 per cent moisture, 10.44 per cent ash, 35.95 per cent volatile and 44.13 per cent fixed carbon. It cost \$5.35 per ton. The equivalent evaporation per pound of dry coal was 10.1 pounds. The cost of coal to evaporate 1,000 pounds of water from and at 212 degrees was 29.2 cents. The average gas made in the producers during the test was typical for Illinois coal and is as follows:

CO <sub>2</sub> .....	4.8
Illuminants.....	0.7
O <sub>2</sub> .....	0.2
H <sub>2</sub> .....	13.5
CO.....	20.9
CH <sub>4</sub> .....	2.0
C <sub>2</sub> H <sub>6</sub> .....	0.8
N <sub>2</sub> .....	57.1
B.t.u. low value.....	144.8

This installation has been in operation 7 years; one of the others has been operating 8 years. The boiler tubes are free from soot and fly-ash, and so is the neighborhood.

From the above test, we may conclude that where only a few hundred boiler horse-power are required and producer gas is available because of large quantities being used in near-by industrial furnaces, it is advisable to fire the boiler with producer gas. It will usually save a third of the fuel and most of the labor.

Although both of the foregoing applications of producer gas are at present limited to units of not over 200 h.p. and have neither superheater nor economizer, they nevertheless compare favorably with modern plants of ten times their size, and consequently are worthy of serious consideration. If the efficiency is higher in small units than conventional practice, it should not be a difficult engineering problem to build larger units having still higher efficiencies.

The chief drawback to progress along this line has been the lack of a suitable gas producer that would meet the special requirements for this new service. Such a producer seems to be at hand. The author is convinced from recent experiments that the following requirements which he believes are essential for the economical application of producer gas to boiler firing in large units, can now be met.

1. The producer should have a maximum capacity of at least 100 pounds of coal per square foot per hour.
2. The cost of the producer equipment should not exceed the cost of competing equipment.
3. The producer should gasify the cheapest fuel known—slack bituminous coal.
4. The producer firebed should be maintained in good-gas-making condition automatically, and require no hand manipulation.
5. The producer should require little or no steam mixed with the air blast.
6. The producer should be adapted to be located directly beneath the boiler and hence no producer top should be required—for attaching the feeding and agitating mechanism.

Although no producer now on the market possesses all of these requirements, the author has met each one of them individually during the past three years, and he sees no obstacle to combining them in a single unit. If this can be done successfully it will make possible another way, and in many instances a much better way, of

firing boilers. For gaseous fuel, since it is in the free molecular state, is superior to fuel in either the liquid or solid state in that it makes possible two-stage combustion.

It is easier to burn producer gas at a rate of 250,000 B.t.u. per hour per cubic foot of combustion chamber than it is to burn pulverized coal at 25,000 B.t.u. per hour. This is largely due to the difference in size of the burning particles. The average size of a particle of finely pulverized coal is as much larger than a molecule of gas as a sphere 1,000 feet in diameter is larger than a pinhead. The very evident advantages of 200 mesh coal over 100 mesh may be taken as evidence of the still greater advantages of the many-million-mesh molecule of gas.

Gaseous fuel will make possible a better design of boiler,—more efficient, simpler and cheaper. If the world had never known any fuel but gas, we would never have developed our present type of boilers. We probably would have built a boiler around a flame, or divided the flame into several parts and surrounded each one with a portion of the boiler, instead of locating the major portion of the boiler as at present, remote from the combustion chamber and beyond the radiant-heat screen formed by the first row of tubes. No doubt we would also have observed the first law of efficient heat transfer from gases to solids and passed the hot gases downward instead of upward while giving up their heat. Let us therefore have an open mind, free from prejudice and the bias of ancestral customs, as we consider this proposed new method for firing boilers.

The Spencer-Bonecourt "Kirke" patent boiler is the first serious attempt we know of to design a boiler for gaseous fuel. It is of the horizontal fire-tube type. Gas is burned in a separate flame in each individual tube by a special multi-jet burner. The overall guaranteed efficiency of gas to steam is 85 per cent if the air is not preheated, and 90 per cent if the air is preheated. No economizer is used.

Twenty years ago the author experimented with a single boiler tube 4 inches in diameter and 16 feet long, firing it internally with washed producer gas made from a low-grade anthracite. By putting the gas and the air under a pound pressure each, it was possible to develop 36 h.p. from the one tube, or approximately 77 pounds evaporation per square foot of fire-tube area. Only with gas can such capacities be attained. The heat generated per cubic foot of combustion space was approximately 1,250,000 B.t.u.

The first of the producer requirements above enumerated is that a successful producer for firing large boilers should be able to gasify 100 pounds of fuel per square foot per hour. Hand-operated producers are limited to one-tenth that amount, and most mechanical producers are limited to half that amount; but by increasing the rate of agitation and either air-cooling or water-cooling the portion of the walls surrounding the hot-zone of the firebed, it is possible to double present capacity and gasify 100 pounds per square foot per hour. (Very few stokers are operated at capacities in excess of ordinary gas producer practice and 60 pounds per square foot per hour is generally considered the limit.) During the past three years the author has obtained capacities in excess of 100 pounds per square foot per hour with three different designs of gas producers.

The second of the requirements enumerated is in regard to comparative cost. The total equipment for producer gas firing would cost less than for pulverized coal, but somewhat more than for stoker firing. A gas producer having a capacity of 8,000 pounds of coal per hour, complete with all accessories, can be built and sold profitably at \$13,000,000 f.o.b. point of manufacture, or about \$6.50 per horsepower. The cost would be somewhat less if the producer walls were supplied by the boiler. Larger sizes would doubtless be built eventually, costing less per unit of capacity. In most cases the labor required for producer gas firing would be the same as for stoker firing, except that gas firing would require much less labor for repairs. Producer gas would of course require no special water-cooled furnace walls and practically no wall or grate repairs. If the producer were built under the boiler and made a part of it as a stoker now is, the cost of the producer gas equipment should compare very favorably with the cost of the best stoker equipment.

The third requirement is that the producer should handle slack coal. The gas producers now on the market have feeding devices that are not suited to handling fine coal. The fuel is fed in by dropping it upon the firebed from a point 5 to 7 feet above, which permits the draft of the out-going gases to entrain the coal dust and carry it away before it is gasified. The author believes that the best way to charge slack coal into a gas producer is by means of a centrally located underfeed. Underfeeding causes the fuel to partially stick together before it reaches the top of the firebed, thus preventing excessive carry-over.

About a dozen experimental underfeed gas producers were built

in this country during the decade that followed the St. Louis Exposition in 1904. Several of these experiments succeeded in making from slack bituminous coal a gas free enough from tar and oil vapors so that it could easily be scrubbed sufficiently clean for use in gas engines. But none of them was a complete success. All failed to produce a reliable and a uniform gas continuously from bituminous fuel, and ultimately they were abandoned.

Two of these underfeed experiments of fifteen years ago attempted to mechanically agitate the firebed, but at that time little was known about mechanical conditioning of producer firebeds. One of these experiments was made by the Ford Motor Company, and the other by the Chapman Engineering Company. If we had known then as much as we know now about firebed agitation, both of these experiments would probably have been successful and today the most popular type of gas producer would be a suitably agitated underfeed producer making a comparatively tar-free gas from slack coal.

Heretofore underfeed gas producers using slack coal and having a vertical feed in the axis, have made the firebed objectionably conical in form—too thick in the center and too thin around the walls. Recently the author built a small underfeed producer which apparently has solved the problem of maintaining a level top in producer firebeds of the underfeed type. Further information upon experiments now in progress is reserved until a later date.

The fourth requirement is automatic operation. This has already been accomplished in our best mechanical gas producers. Some of them require no hand manipulation of the firebed at all. The usual length of run without stopping is from six months to a year, which is far better than either stoker or pulverized coal practice. The author believes that it will not be difficult to apply to underfeed practice the best forms of agitation now employed in top-feed producers.

The circular shape of a gas producer lends itself to mechanical feeding, mechanical agitation, and mechanical ash removal. These functions are best performed by rotary motion. The square shape of a stoker grate is not adapted to rotary motion, and the use of a suitable agitating member in a square firebed is impractical. A thin firebed will not be benefited by an agitating member, and if the firebed is sufficiently thick to be properly agitated it will be thick enough to make a considerable amount of producer gas; hence, the logic of two-stage combustion.

The author has burnt washer refuse (called "bone coal," by courtesy) that contained over 7 per cent sulphur and over 50 per cent ash, at the rate of 110 pounds per square foot per hour, in a circular gas-producer-agitated firebed, and obtained a stack gas averaging over 17 per cent  $\text{CO}_2$ . Such results are utterly impossible with any type of stoker or pulverized coal equipment on the market today. Only in a circular firebed is it practical to obtain the agitation required for such low-grade fuels. The gas producer which the author proposes might be considered merely an improved form of underfeed stoker with an extra thick firebed having special agitation at the bottom and secondary air at the top—a sort of adaptation of gas producer practice to stoker practice, in fact a special stoker for two-stage combustion.

The fifth point is the use of a minimum of steam in the air blast. The steam required usually represents 3 per cent of the coal gasified. (Producer gas practice should not be confused with Mond gas practice, which frequently requires ten times as much steam.) When gasifying the refuse noted above, no steam whatever was used in the air blast. However, a slight amount of steam in the blast does not seriously impair the efficiency of a deep, hot, producer gas firebed, for if the fuel is hot enough, substantially all of the steam will be converted into hydrogen and oxygen. On a properly designed producer the loss in efficiency due to steam required in the air blast can be kept down to 1 per cent. Moreover, the introduction of a small portion of the hot stack gases may be substituted for steam in the blast if desired.

The sixth point is that the producer should have an open top so that it may be located directly under the boiler. This requirement is well met in the underfeed type of producer already alluded to. Not every type of underfeed however would be suitable. A lop-sided firebed cannot be used. The oblong shape of the conventional underfeed stoker renders it impossible to feed the fuel symmetrically. It has been tried a number of times in gas producer experiments and has always failed to produce a uniform firebed. Uniform gas is essential and it cannot be made in a non-uniform firebed. The fuel and blast in an underfeed producer flow in the same direction at the start. This does not permit the fuel to be burned up completely without excess air. It is therefore necessary that the upwardly moving fuel be made to reverse its direction of flow and thus oppose the stream of incoming air in order to be com-

pletely consumed. The deep circular firebed of the gas producer makes this type of underfeed fuelbed easily attainable.

None of the six requirements discussed above appear formidable to the author. They can all be met in a properly agitated underfeed type of producer of symmetrical construction.

They were almost met in the 10-feet-inside diameter underfeed producer built and operated by Henry Ford fifteen years ago. It was designed by Edward Gray, Ford's chief engineer at that time. It, however, had no agitating member but relied upon a twisting action in the firebed caused by revolving the lower bosh-like portion of the producer walls. The agitation so produced did not prove to be sufficient to break up large clinkers when once formed, and the results obtained therefore lacked uniformity.

Pulverized coal firing is generally considered more efficient than stoker firing because less excess air is used and less carbon is lost in the ashes. Producer gas firing would save even more of the carbon in the ashes, and furthermore it would require only one-third the amount of excess air now required in pulverized coal practice. It is not difficult to burn producer gas completely while maintaining the excess air at about 5 per cent. Producer gas should therefore be slightly more efficient than pulverized coal.

The easy control that makes possible a quick response to large changes in load in pulverized coal firing is perhaps its outstanding advantage over stoker firing. Producer gas made from a deep firebed will respond with equal flexibility to sudden changes in load. Whether the quality of the gas be good or bad, the primary air required below the firebed to generate the gas plus the secondary air required above the firebed to burn the gas will always be the same per pound of carbon consumed. Hence, a sudden and large increase of air to meet a sudden demand on the boiler will immediately produce a corresponding increase in heat. It is not necessary in producer practice to increase the amount of fuel on the grate before the rate of combustion can be increased, as is the case in stoker practice, for in a gas producer the firebed is always deep. The gas may not be quite as good in quality for the first five minutes after the air rate has been suddenly increased 500 per cent but any loss in quality is always offset by an equivalent increase in sensible heat of the gas, and the net result is a flexibility approximately equal to either pulverized coal or atomized oil. In the Wollaston producer-boiler already alluded to, it is the custom to obtain full steam pressure after a week-end shutdown in fifteen minutes Monday mornings.

One of the most important advantages of two-stage combustion is that less than half the air is used in the first stage. If the volume of the gases passing through the solid firebed is cut in half the amount of fines lifted out of the firebed (which varies at a little greater rate than the cube of the velocity) will be reduced to about one-tenth. Two-stage combustion also is adapted to use highly preheated air. At least half of the air could be heated to any temperature desired.

In regard to the question of carbon in the ashes, the gas producer has considerable advantage, for in a gas producer the fuel and air flow in opposing streams, as they should. In a stoker the fuel and air flow at right angles, making it impossible to accurately regulate the coal feed to agree with the draft. In pulverized coal practice they flow in the same direction. When the coal and air flow in opposing streams, no such problem of accurate control exists, and the carbon in the ashes is easily kept below 5 per cent, representing a fuel loss of about 0.5 per cent.

In conclusion the author urges all power plant engineers to get acquainted with producer gas and keep in touch with improvements in mechanical gas producers, for therein lie immense latent possibilities for obtaining more steam for less money.

# THE RATIONAL UTILIZATION OF COMBUSTIBLE GASES

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## GENERAL CONSIDERATIONS

The ease with which one can economically and safely transport industrial gases under pressure or in liquid state, thanks to the modern methods described in our article entitled "The Transportation of Industrial Gases," makes it possible to derive greater profit from certain combustible gases by ceasing to consider them as more or less flexible or efficacious lighting or heating agents and as a base for some syntheses.

The new uses will certainly bring about a marked improvement in the economic yield of the following manufactures: (1) synthesis of ammonia, (2) transformation of derivatives of ethylene into alcohol, (3) synthesis of methylene- and homologous alcohol—this notably in countries like France which do not use petroleum, as well as in countries where natural gases are abundant.

The syntheses which have just been indicated can be realized only after the removal of all trace of benzole, and complete elimination of the sulfur derivatives which are always more or less abundant in the gases utilized but which, if present, even in weak proportions, often play a very harmful rôle.

It is therefore necessary to treat especially coke-oven gas with care in order to remove from it the hydrogen which is at the base of the synthesis of ammonia, whatever be the method employed otherwise.

Among the combustible gases whose utilization we are considering one may cite: city gas or coke-oven gas with 4,500 calories per cubic meter; methane with 9,000 calories.

The treatment of a ton of oil furnishes a mixture of methane and of these six gases in variable proportions, the total volume of which reaches 350 to 450 cubic meters, according to the studies of Professor Mailhe and the experience with a recent installation.

All the residual gases of high thermic potential resulting from the treatment of heavy oils by the so-called "cracking" methods such as:

	<i>calories per cubic meter</i>
Ethane giving.....	16,200
Propane.....	23,000
Butane.....	29,000
Ethylene.....	13,600
Propylene.....	20,400
Butylene.....	27,200

Since these gases are capable of undergoing without any danger, except perhaps for ethylene, pressures as great as 500 kgm. per square centimeter when their oxygen content does not exceed from 2 to 6 per cent, one can see that it is much more desirable, their thermic potential being given, to use them for quite a different purpose from the heating of ovens, various apparatuses, etc., these operations being taken care of by using more economical agents such as gas from gas generators, water, gas, etc.

#### CHARACTERISTICS OF CERTAIN GASES

The complex operations necessitated by the majority of synthesis effected industrially at this time (fractionation by compression and expansion, purification of the fractions, transformations in the presence of catalytic agents under pressure, etc.), make it particularly advantageous to treat the gases simultaneously. Nevertheless, there always remains a residue of gases which are absolutely refractory to these reactions. These are the saturated hydrocarbons to which may be added a greater or smaller ballast of nitrogen.

These hydrocarbons may be, in their turn, submitted to a condensation capable of giving liquid products; we may expect that in case we should succeed in obtaining by this method a suitable industrial yield, we would certainly approach natural petroleum; and that is the need of tomorrow.

Up to the present time, it seems that we have run afoul of the very character of ethane and of methane which, already saturated, show only a very weak capacity for uniting in longer chains.

In the syntheses which we have enumerated, these hydrocarbons constitute, to a certain extent, a waste; on the other hand, they constitute from the calorific point of view a concentrate of very great value.

When these gases are obtained by the distillation of combustibles at high temperature, the content of saturated hydrocarbons varies between 5 and 25 per cent; when one operates by distillation at low temperature, this content frequently reaches 60 per cent starting with carbons and schists and becoming considerably lower when one is treating lignites. Moreover, it is found in this case that the proportion of propane is negligible and that of methane is much greater than that of ethane.

We contemplated, especially for low-temperature gases, a partial utilization under a form which at the beginning seemed quite attractive; it concerned the condensation into a liquid of weak density (about 0.65) of all the elements capable of assuming liquid form under a moderate pressure, and which corresponded to the fractions which under atmospheric pressure begin to boil within the limits of 40° to 100°C.

Nevertheless, this liquefaction by simple pressure only concerns a small portion of the residual gases, so that the problem of utilizing the methane remains unsolved. It is necessary to point out that the very extensive use of these liquefied gases in Germany under the name of Blau gas, Wolf gas, Gasol, etc., has resulted in disappointments.

Indeed, at the time of expansion, there is produced a fractional evaporation causing constant variations in the nature and the properties of the gas in proportion to the exhaustion of the contents of the cylinder, and therefore one cannot work regularly, especially in autogenic soldering, with a combustible of this nature.

The various syntheses deriving from methane do not seem to have given, from the point of view of yield, very encouraging results; its transformation into hydrogen by heating or catalytic oxidation does not utilize it completely and is quite costly; it is therefore necessary to use it in another way if one wishes to give it a value in excess of its thermic potential.

As for ethylene, slightly endothermic, and presenting on this account certain dangers when it is put into a cylinder under pressure, its transformation into ethyl alcohol is an established fact, but the small quantity of coke-oven gas that one can extract from it (perhaps 2 per cent at the most) does not allow it in France to supply a large market; one can recover 8 liters of alcohol per ton of distilled coal.

On the other hand, thanks to the use of suitable catalytic agents,

the syntheses deriving from carbon monoxide have assumed an industrial importance which has not failed to attract considerable attention.

We may therefore conclude that, for the time being, it is not in the process of syntheses nor in that of heating that we must consider the more remunerative utilization of saturated hydrocarbons with increased thermic potential.

We must therefore as R. Brunschwig, Engineer-in-Chief of Mines, said in his very remarkable lecture on "Synthetic Fuels," seek to benefit from their chemical compactness resulting from their saturated union, without destroying them. We are going to define some uses which will lead the producers of these residual gases to derive from them a very valuable yield for the total of their operations.

#### *A. Utilization for Automobile Propulsion*

In order not to make this discussion too long, we shall only concern ourselves with city gas, coke-oven gas and methane.

All three constitute fuels capable of being used for the propulsion of heavy motor vehicles which return each evening to their point of departure after having made a set trip. In this respect, city gas and coke-oven gas have the same technical value. Coke-oven gas is also a remarkable source of hydrogen, having a residue of methane mixed with ethylene, carbon monoxide, and nitrogen after the carbonic acid has been totally removed.

As for methane, not only does it constitute an especially interesting fuel, but in addition, it is recommended for raising the thermic potential of certain industrial gases the use of which would then spread.

In order to transport these gases, as well as natural gases which contain a very large proportion of methane after the removal of the more volatile part, it was important to effect simple, safe and light packing; this question having been treated elsewhere, we do not have to return to it; in the following statements we shall take as our basis the figures furnished in our article entitled "The Transportation of Industrial Gases."

*City Gas.* As early as 1902 in France, they attempted to feed automobiles with city gas, this utilization was resumed during the war and has only been seriously considered since the appearance on the market of light set of cylinders capable of constituting gas reserves at high pressure, of considerable volume and with a minimum weight.

At the present time, the Societe des Transports en Commun de la Region Parisienne, as well as several gas companies, have equipped vehicles or locotractors for experimental purposes utilizing city gas; a recent road test organized and controlled by the Automobile Club of France established the fact that two autobuses equipped with gas were able to travel almost 2,000 kilometers on the roads of the East, the North and of Belgium consuming from 650 to 700 liters of gas at 4,500 calories per kilometer-vehicle according to the sections, and at an average speed of 24 kilometers per hour, or 65 to 70 cubic meters per 100 kilometers.

The same vehicles consuming 38 to 40 liters of liquid benzole per 100 kilometers, the savings resulting from the use of gas is far from negligible.

When these two vehicles could be fed with gas of higher thermic potential, the consumptions were reduced. In the course of the Mons-Bruxelles trip, since it was possible to supply one of the two autobuses with gas with 7,550 calories, the consumption was reduced to 330 liters for an average speed of 28 kilometers per hour; the same discovery was made on the Bruxelles-Liege trip where the consumption was 325 liters. The 4-cylinder motors with which these autobuses were equipped had the following characteristics:

Bore (internal diameter).....	110
Piston stroke.....	150
Speed.....	1,250 revolutions
Compression.....	5.1

This compression could not be permitted for gasoline, but benzole and alcohol adapt themselves to it perfectly.

Mr. Castaing, Chief Engineer of the Services de la S. T. C. R. P. had previously declared in his report as follows:

"Successive readjustments of the mixing apparatus have made possible in the course of more recent experiments (1) a consumption of 0.632 cubic meters of gas (with 4,500 calories per cubic meter) per kilometer-vehicle as against 1.400 of mixture oil of benzol 8,240 calories per liter (2) under similar conditions.

"The specific consumptions in calories respectively are then: 2,850 calories for the gas, against 3,290 calories for the mixture of equal parts of oil of benzole and heavy oil.

"One may therefore admit that the minimum economy of 10 per cent in calories in favor of the gas in comparison with a volatile liquid

combustible pointed out by various authors, and especially by Mr. Alfred Bazille (3) is practically verified."

The savings in calories are, therefore, considerable; it is certain, moreover, that they will be still further increased when the technical character of automobile motors using the gases shall have been definitely determined, as regards rate of compression, lead to the ignition, feeding, and filling of cylinders, cooling, form of the explosion chambers, etc.

From the point of view of the packing weight, the comparison between gasoline and gas may be made by taking as a basis:

- (a) The calorific power of the gasoline, let us say 8,050 calories per liter
- (b) Its density, let us say, 0.730
- (c) The average consumption in calories per CV horsepower hour, let us say 2,500 calories, this last element representing a thermodynamic yield of 25 per cent which is not at all excessive, and which will certainly be high in an explosion motor specially conditioned to run by gas.

A liter of gasoline of 8,050 calories stores 3.220 horsepower hours, the total weight is about 1 kgm., that of the combustible being 730 grams, the total weight per horsepower hour therefore amounts to 312 grams, including the weight of the combustible.

- (1) The service effected was that of a normal truckage service at the S. T. C. R. P.
- (2) Benzole 90 per cent washed (D-0 .88) lower calorific power: 8,435 calories per liter
- (3) *Journal des Usines a Gas*, April 20, 1927.

A cubic meter of city gas contains 1.8 horsepower hour; put up in flanged tubes weighing 5 kgm. per cubic meter, the dead weight amounts to 2.770 kgm., whereas put up in a commercial tube of 50 liters in water containing, 7,500 liters of gas at a storage pressure of 150 kgm. weighing 10.300 kgm. per cubic meter, the dead weight would amount to 5.600 kgm., the gain, say of about 50 per cent is therefore considerable. Moreover, the flanged cylinder makes it possible to approach the pressure of 200 kgm. without any disadvantage, all of which improves considerably the preceding conditions based on 150 kgm.

It is unnecessary to stress the considerable interest for manufacturers of the use of compressed city gas for heavy automobiles and those making regular trips, such as trucks, autobuses, delivery vehicles, etc.

From the point of view of gas companies, they will find in this new outlet a great improvement of the efficiency of their factories, as well as a considerable source of profit, the gas destined for feeding the motors being taken on the spot, without any expense of distribution by pipe-line, and consequently without any additional expense due to leakage in the pipes.

As for the compression of city gas at 200 kgm., the conditions under which it can be effected have been studied at length by Professor James Chapuis, director of the Services des Recherches Physiques de la Societe du Gaz du Paris, and his assistant, Mr. Pignot, Docteur des Sciences.

This remarkable study was the subject of an article read at the Academies des Sciences, December 19, 1927.

In short, to compress a cubic meter of gas sucked in by atmospheric pressure to 200 kgm., it is necessary to apply to the compression pulley a force of 72,000 kilogrammeters corresponding to an efficiency of 65 per cent for the compressor, which represents 0.3 horsepower hour, an insignificant expenditure; 20 centimes per cubic meter for expenses of compression is normal.

City gas is therefore a substitute fuel, the use of which can be profitably arranged for in every city possessing a production factory or an accumulating gas tank receiving gas transported by pipe-line.

*Coke Oven Gas.* From the point of view of automobile propulsion, all the figures which we have just given with reference to city gas, as well as our conclusions, apply also to the use of coke-oven gas; it is therefore recommended to use it as a fuel since that is more profitable than to sell it, even on the spot, as illuminating gas.

If one transports it at a distance by means of modern pipe-lines, this is less profitable since it is necessary to take into account the leakages, the expenses of compression, etc.

Used for operating stationary gas motors, it is still unprofitable because one could employ a motive agent less expensive such as gas-generator gas or water gas.

Therefore, the utilization of coke-oven gas is highly recommended as a substitute fuel, either directly, or as residual gas of synthetic manufactures, of which we shall speak a little later.

Indeed, if one considers heavy gasoline giving 8,050 calories per liter and costing 1 franc 80 centimes a thousand calories would cost 22 centimes 3.

The equivalent per cubic meter for gas of 4,500 calories is therefore

1 franc 3 centimes; if one desires to allow the user a very large profit of 40 per cent in comparison with gasoline, it will be necessary to deliver the gas at 0.60 centimes per cubic meter at the factory, compressed at 200 kgm. in flanged cylinders belonging to the purchaser, and fixed on his vehicle or in accumulator pressure reservoirs.

We have indicated that the expenses of compression do not exceed 20 centimes per cubic meter, including the upkeep of the plant, its liquidation, and the incidental expenses for an installation of 50 cubic meters per hour.

Under these conditions there will remain to the coke-oven operator 40 centimes per cubic meter, representing a recovery of at least 48 francs per ton of coke, conceding a surplus of 120 cubic meters of gas, after deducting the quantity used in heating the ovens.

Engineer-in-Chief Brunschwig has estimated at 800,000,000 cubic meters the quantity of gas produced by the coking plants of the mines in France, in addition to the volume used in heating the ovens. The same author has pointed out that by heating the ovens with poor gas one would liberate about a billion and a half of cubic meters.

These two quantities, or 2,300,000,000 cubic meters would represent, on the scale of 1.4 cubic meters of gas per liter of gasoline, about 1,920,000 tons of gasoline, or nearly twice the present French consumption.

On the other hand, the synthetic manufacturers having hydrogen for a base have opened the way to a very remunerative use of coke-oven gas, especially if one uses methane and the gases allied with it as substitute fuel.

It is a known fact that the extraction of hydrogen from coke-oven gases is accomplished either by means of liquefaction at very low temperature by the Linde or Claude processes, or by passing steam over the red-hot iron, and next reducing the iron oxide thus formed by the coke-oven gases.

By the first method, and for a well regulated manufacture, permitting an adjustment of the ratio of pressure in the different parts of the apparatus, one obtains with continuous operation, gases containing as high as 96 per cent of methane.

One can therefore, by treating 2 cubic meters of coke-oven gas, obtain at least one cubic meter of hydrogen, and 400 liters of methane with an expenditure of from 0.3 to 0.5 horsepower hour for an installation capable of treating 700 cubic meters per hour.

If, therefore, one recovers the methane, one will reduce to a very

great extent the net cost of the hydrogen, and consequently of the ammonia, of the hydrogenation of the oils, and of the coal by the Bergius process.

One can see by the preceding statements the profit one can derive from coke-oven gases used directly as fuel or as manufacturing agent of hydrogen with a recovery of methane and its allied gases, as well as a recalisator of gases having weak thermic potential, subsequently used as city gas for example.

Of course, the hydrogen must be utilized on the spot, because it is not economically transportable in high-pressure containers due to its properties.

As for the methane, it is very easily transported, either in containers which are flanged, and consequently light, or in liquid state in the special cylinders described elsewhere.

*Methane, or Natural Gases, or Residual Gases with a Predominance of Methane.* We are going, at the very outset, to consider the use of methane with 9,000 calories as a substitute fuel. By reasoning as we did in the case of city gas, and by taking the same bases, we arrive at the following figures:

Number of horsepower hour in a cubic meter of methane . . . . .	3.6
Weight per horsepower hour of the flanged cylinder . . . . .	1,380 kgm.
Equivalence per liter of gasoline . . . . .	6 to 700 liters

One can see that, with fixed equal weight, it is possible to effect a kilometric trip twice as great with methane as with city gas or with coke-oven gas.

By the same reasoning, the equivalent of the price of methane with 9,000 calories in comparison with heavy gasoline with 8,050 calories, costing 1 franc 80 centimes per liter is 2 francs per cubic meter. If as before, one leaves a margin of profit of 40 per cent for the user the cubic meter will be delivered at the factory at 1 franc 20 centimes, or deducting expenses of packing by compression or by filling a weight of liquid methane in a cylinder of known capacity, 1 franc per cubic meter taken at the factory.

For coking plants using hydrogen extracted from their gas, one can find in the recovery of methane a very considerable revenue.

Indeed, let us suppose that one obtains 280 cubic meters of gas, of which a minimum of 120 will remain as available surplus containing 25 per cent of methane; one will recover 30 cubic meters of methane corresponding to a reduction in cost of the coke of 30 francs per ton, not including the income from the sale of the hydrogen.

It is well to recall, that methane is 25 per cent more compressible than is indicated by the law of Mariotte Boyle, and that this situation which is very favorable has not been taken into account in the preceding calculations; thus the fixed dead weight will be proportionately diminished.

As for the utilization of gases, the thermic potential of which is between 5 and 9,000 calories per cubic meter, the same reasoning is applicable to them in every respect.

Moreover, road experiment has demonstrated the fitness of these gases for automobile propulsion; in that respect it is the best use of their properties.

In addition, in the course of the road experiment previously discussed, there was used with absolute success a residual gas resulting from the extraction of hydrogen from coking plant gases having the following composition:

	<i>per cent</i>
Methane.....	72
Hydrogen.....	5
Carbon monoxide.....	10.8

and whose calorific power amounted to 7,750 calories per cubic meter.

*Other Saturated Gases.* We will say only a few words concerning the other gases mentioned at the beginning of this article. If they can be used as recolorizator agents, it does not seem that from the point of view of a substitute fuel they can be compared to methane and be as profitable as it.

Indeed, and until a series of practical experiments shall have been able to determine the conditions or normal use of gases of more than 10,000 calories per cubic meter, it seems that their inertia, probably due to their chemical composition, is an obstacle to obtaining a yield proportionately higher, all other things being equal, than with methane. On the other hand, one of the causes of the reduction in yield seems to be the great quantity of air which must be introduced to insure their complete combustion.

*Apparatuses for Utilization of Gases.* The reserve gas installed on a vehicle equipped with a pressure gauge having been calculated quite liberally in order to insure a given trip, it is necessary, in order to utilize it practically, to have recourse to the following apparatuses: Pressure expansion regulator and gas mixer-carburetor.

The technical character of the first of these apparatuses has been well known since the spread of autogenic soldering; nevertheless, in

the case occupying our attention, it is necessary to use extremely sensitive pressure regulators, in spite of an essentially variable flow. Experiment has shown that to attain this goal, the diaphragm of the pressure regulator must have a large surface; the apparatuses constructed by the Societe des Tubes Frettes having a large diameter have given complete satisfaction not only in experiments, but also during road tests to which they were subjected.

As for the mixer-carburetor, the same company has made apparatuses, the functioning of which has been recognized to be perfect; at the present time improved apparatuses are being studied, the automatic quality of which will be absolute under all conditions.

### *B. Gas Locotractors and Locomotives*

The use of gases for railroad traction is highly recommended especially for locotractors with the normal track of mining operations possessing coking plants, as well as in the railroad systems with narrow track where the expenses of steam locomotive traction absorb the greater part of the receipts.

The gas locomotive of direct control or that of electric control will make a paying proposition out of certain deficient departmental works by using city gas; these same works will give to the gas factories situated at the terminals or along the way receipts which will not be negligible.

Without speaking any more at length about the subject we call attention to these particularly important applications of which we have made an intensive study.

*Gas Generators Placed on Vehicles. Comparison of installation weights.* We could not close this chapter on the use of gases for automobile propulsion, stored and transported on the vehicle itself, after having been made in factories, without saying a word about the use of gases produced on the vehicle itself.

This idea is already old, because in 1906 the English engineer Thornycroft presented to the Naval Architect a study on the application of poor-gas motors to navigation by means of installations of 500 and 1,000 CV (horsepower) for the propulsion of a cargo of 7,000 tons.

In 1908 and 1909, Mr. Schmidt and Mr. Cazes presented, each on his own part, automobile trucks run by poor gas.

Since then, numerous builders have put on the market similar installations fed with wood charcoal, wood, lignite, peat coal, as well as with special agglomerates such as carbonite, synthetic carbon, etc.

In spite of certain economic and fiscal advantages, these various systems have not been developed as one might believe. So it is, for example, that French statistics indicate the existence on Dec. 31, 1927 of:

Small and large trucks.....	306,452
Tourist vehicles.....	642,744
Cyclecars.....	27,450
Pleasure automobiles.....	3,313
Motor cycles.....	232,201

Out of this great total, gas-generator vehicles, although paying only half tax reach only the insignificant number of 365.

The reasons for this poor development are many. The savings are offset to a great extent by a considerable expenditure of lubricating oil, by an increase in the price of labor due to the limitations of this system, for example, in the starting up in the morning and on the warming up again after stops which have been more or less long, etc.

On the other hand, the weight of all the apparatuses for the preparation of the gas, the purifying, filtering and cooling which, during 1924 was 450 kgm. on an average, has at present fallen to about 300 kgm.

If we consider a heavy truck, whose motor normally delivers 25 horsepower, or en route 65 per cent of this power or an average of 16 horsepower, the total weight of a gas generator installation supplied with wood will be:

Weight of the total installation.....	320
Consumption of 1 kgm. of wood per horsepower hour.....	16
<hr/>	
Total.....	336

The dead weight per average horsepower hour is  $\frac{336}{16} = 21$  kgm. and  $\frac{336}{25} = 13,400$  kgm. delivered power.

Equipped with methane gas, the weight of the installation would be about 120 kgm. by using flanged tubes; the rendering immovable in weight with the gas-generator installation is therefore considerably greater than that of the equipment using methane.

### *C. Recalorization of Gases Having Weak Thermic Potential*

It is easy to realize from the foregoing statements the interest which is attached to the use of gases for automobile propulsion. It insures a considerable value to by-products in the carbonization

factories, improves their financial return and may even go as far as permitting the development of carbonization at low temperature which up to the present time has been a poorly paying enterprise in the majority of cases.

On the other hand, the enrichment of certain gases having weak thermic potential by methane and certain saturated hydrocarbons in gaseous state assures, since the problems of transportation and packing are solved, a considerable market for these gases.

It is a known fact, that the manufacture of city gas, especially in France, has the tendency to evolve towards the increase in the yield of gas and the decrease in the production of coke from gas.

The engineer A. Grebel published in 1925 a very documentary study on this important question; he determines with precision the rational limit of the production of coke by pointing out that a gas factory ought never to produce more coke than is normally asked of it on an average.

To attain this goal, a gas factory will have to make water gas, but since it is bound by the regulations not to exceed 15 per cent of carbon monoxide, the transformation of the coke into water gas, which is entirely justified because the coke is better utilized thus than in solid state, is of necessity limited.

The problem assumes quite a different aspect if one uses methane or cheap natural gas which can be easily transported in a gas factory in liquid state for example.

Indeed, one will limit the distillation of the coal to a suitable tonnage; that done, one will manufacture with a part of the coke obtained, water gas of about 2,800 calories; then one will enrich a suitable proportion of the quantity of water gas thus manufactured in order to obtain a gas of 4,500 calories.

Under these conditions, in order to meet the needs of its output, the factory under consideration will have at its disposition:

- (a) A determinate quantity of first distillation coal gas giving about 5,000 calories per cubic meter.
- (b) A quantity of water gas giving about 2,800 calories.
- (c) Liquid methane of outside provenience which it will use to recolorize the total mixture of coal gas and water gas.

Therefore, for the same total volume of gas delivered, the factory will have distilled less coal and consequently produced less coke; it will utilize a portion of this coke in the manufacture of the necessary volume of water gas, and it will sell the remainder.

There is every proof that a combination of this sort will be all the more advantageous as the proportion of water gas admitted into the city gas is increased.

In France where this proportion, for the time being at least, must not exceed 15 per cent of carbon monoxide, the economical combination which has just been developed is less advantageous than in the countries where one can mix as much as 25 per cent and even more water gas with the city gas.

It would be impossible to use alone either methane, or natural gas, or the residual gases having a great predominance of methane, as illuminating agents, unless one adopted an equipment specially suited for this purpose, which would lead to prohibitive expenses for the installations now existing.

These various gases all possess, from the point of view of their combustion, the defects of their principal component, methane; they must therefore be made poorer and improved by means of mixture with gas having a high content of hydrogen and carbon monoxide such as water gas; Mr. Grebel has perfectly explained this point in his study.

Therefore, the gas factories situated in certain centers producing methane will be able to receive economically by automobile or by wagons in rapid rotation the quantities of methane or rich gas necessary for a composite manufacture, thus causing a considerable reduction in the tonnage of salable coke; there will follow for the producers of methane and of rich gas large profits.

#### *D. Autogenic Soldering—Producing High Temperatures*

To be complete, it is well to point out that, especially in Germany, they have considered the use either of methane, or of a mixture of methane and ethylene in special blowpipes with a mixture of oxygen for the production of high temperatures and the autogenic soldering of the metals; many patents have been taken out, especially by the Rombacher Huttenwerke and Mr. Jegor.

It does not seem that for the time being at least we have arrived at questionable practical results; nevertheless, these various processes are still under study. They will have to win the position taken by acetylene in this important domain of industrial technique.

## CONCLUSIONS

The ideas which we have just set forth, easy to put into practice, under conditions of remarkable simplicity and safety, will improve the synthesis industries, the gas industry, and the national economy of the countries which shall use them.

Indeed, whatever be the position of a nation as regards the problem of fuels, it is contrary to all spirit of economy to allow calories to be lost or to use them in a wasteful manner.

At this time when all efforts are bent towards a better utilization of raw material, towards the reduction of cost prices, the saving of calories is by the same token an obligation. There is no country too rich to neglect it; this program must be carried out in all its aspects, but only after deep study of the numerous cases of kind which it comprises. However, it presents no risk as is shown by the lessons one may learn in France, where its putting into practice is being progressively followed out.

# TRANSPORTATION OF INDUSTRIAL GASES

By C. SIMON

*Consulting Engineer, Member of the Board of Directors of the Wire Wound Cylinder Company*

*Presented by Jacques Weiss, Manager of the Wire Wound Cylinder Company*

## GENERAL CONSIDERATIONS

The considerable disproportion which exists in the transportation of compressed, liquefied or dissolved gases between the weight of the container, built to meet certain legal requirements and the weight of the gas or liquid which it contains, has led to a search for more economical solutions with high degrees of safety.

If we consider oxygen and hydrogen, to speak of only these two gases, which can be transported under a pressure of 400 kgm. for the former and 200 kgm. for the latter, while meeting requirements in force in France, it is noticed that a normal container, holding 7,500 liters of oxygen or hydrogen under 150 kgm. pressure, when brought back to atmospheric pressure, weighs with its valve from 76.5 to 77.7 kgm. according to the manufacturer.

As the 7,500 liters of oxygen represent  $7500 \times 1.430$ , or 10.725 kgm., it can be seen that the container weighs 7.7 times more on an average than the available gas.

With hydrogen this difference is still more noticeable, as the 7,500 liters of this gas weigh only 0.6675 kgm., or 112 times less than the container.

It is therefore evident how much this unfavorable condition affects the cost price of these two gases when they are used far from their center of production.

As oxygen and hydrogen follow closely Boyle's law, it is evident that there is interest in storing them under the highest pressure compatible with shipping regulations, as the cost of compression is only proportional to the logarithm of the pressure and not to the pressure itself. However, from an economical point of view, it is best not to go beyond the value for which the product of the pressure and the volume ( $pv$ ) is a minimum at a mean room temperature. Van der Waals' equation makes it possible to determine this value very accurately.

One must, therefore, have recourse to a container which permits

reaching high pressure while maintaining a very high factor of safety by decreasing the weight of the container as much as possible.

The Wire Wound Cylinder Company has developed a container meeting these conditions.

We can, therefore, conclude that the problem of storing of gases under high pressure (100 kgm. and upward per square centimeter) is solved as we shall see by what follows.

Finally the Wire Wound Cylinder Company has studied another patented process making possible the transportation of liquefied gases. We have thus available two processes for the shipment or for the storage of gases; it seems of interest to describe and to compare them, as each one meets a certain number of special conditions. They are moreover characterized as follows:

A. Light wire wound cylinders capable of withstanding very high pressures, making possible the shipment, stocking of gases, their rational industrial utilization, especially for welding, for fitting automobiles with reserves of combustible gases to be used as substitute fuels, and for all installations of compressed air or oxygen aboard submarines.

B. Special receptacles suitable for the shipment, in large quantities, of liquefied simple gases like oxygen, methane, acetylene, etc., without any appreciable evaporation and without the use of vacuum.

These two systems, by placing new means at the disposal of the gas industries, are going to make possible difficult uses, if not impossible till now, on the subject of which we devote a special study entitled "On the rational utilization of combustible gases."

A. *Light Wire Wound Cylinders.*<sup>1</sup> These cylinders, the tare weight of which varies between 4.5 and 5 kgm. per cubic meter of enclosed gas instead of 10 to 11 kgm., are constructed in such a way as to avoid a series of serious objections and to take advantage of the elasticity of the envelope and of the high resistance of the steel wire hoops of from 200 to 250 kgm. at the breaking point, while maintaining very high margins of safety.

A very simple comparison illustrates the process used in advance of any mathematical theory:

All automobilists know that it is impossible to run on inner tubes only, but that the latter resist very high pressures when they are kept in place in the tires held by the rims.

The shell of the wire wound containers constructed of ductile metal

<sup>1</sup> U. S. Patent No. 1,651,521 of December 6, 1927.

plays the part of the air-tight chamber, the longitudinal and transversal hoops that of the tire and rim furnishing resistance.

Instead of having recourse, as is usual, to thick walled and heavy metallic envelopes, we use light and thin walled envelopes by surrounding them with hoops presenting a very high resistance to rupture and made up of high resistance steel wires, the properties of which have been known for a long time. If, in the case of a thin wall container, the sheet iron envelope was given the ordinary circular form of a cylinder resting purely and simply on the transversal hoops and if a high internal pressure was developed in the receptacle thus formed, the wires and the sheet iron would undergo the same expansion per unit of length, since, being in contact, they expand together under the effect of the internal pressure.

The coefficients of elasticity of the two constituents (wires and sheet iron) are close to each other. We may suppose that wires are used where this coefficient will be 20,000 and sheet iron for which it will be 18,000. The wires have an elastic resistance which can reach 240 kgm. per millimeter while that of the sheet iron is very much lower.

If one wishes to utilize entirely the resistance of the wire hoops the construction will be so regulated that under the experimental pressure of the cylinder they will work under a stress of 160 kgm. and will therefore undergo an expansion of 0.90 per cent of their length.

The sheet iron which is in contact with them will necessarily undergo the same expansion, which would correspond to a stress of  $0.90 \times 18,000$ , or 162 kgm. per millimeter if this expansion was elastic.

But this stress of 162 kgm. is far beyond the elastic resistance of the sheet iron, this metal can therefore follow the deformations of the steel wires only by assuming a permanent expansion.

If the plate used is made of a ductile metal it will be able to follow this permanent expansion without rupturing; but when the pressure developed in the inside of the reservoir ceases, the wires, due to their high resistance, having only undergone an elastic expansion, will tend to come back to their original length. The plate which, on the contrary, has assumed a permanent expansion, will tend to keep its new dimensions and will not be able therefore to come back to its initial diameter. It will therefore undergo a very powerful pressure from the wires and will become corrugated.

These phenomena are similar to those produced when a lining is placed inside a gun.

However in our particular case the sheet iron wall is relatively much thinner than in the case of a gun. It is so much more so that in order to manufacture receptacles as light as possible, it is desirable to increase the number of wires as much as possible to support the inner wall which is made of much less resistant soft metal.

The Wire Wound Cylinder Company has solved the problem by giving the inner shell neither a circular cross section nor a longitudinal rectilinear section.

The cross section is slightly undulated and its profile resembles a section of a melon through its equatorial plane (Fig. 1).

When the inner envelope expands under the effect of the pressure the undulations flatten out against the outer system of wire hoops,



FIG. 1



FIG. 2

exactly as the creases of an air chamber disappear under the action of air pressure against the outer shoe which alone assures the resistance of the whole. For the same reason the longitudinal section has two or more transversal depressions (Fig. 2) the profile of which will flatten out under pressure and will allow for an easy expansion lengthwise.

As to the external envelope, it is composed of a double system of wires. Some, directed lengthwise and fairly well separated one from the other, prevent expansion at the ends. The others are coiled above the first ones around the envelope; they are coiled close to each other and prevent the bursting of the sides. Their cross sections are represented by points (Figs. 1 and 2). The interior en-

velope is thus free to expand in all directions and will not assume any permanent deformation.

When a filled container is emptied, the wire hoops will cause the inner envelope to undergo a powerful contraction which would cause its warping if it had a circular cross section and a rectilinear longitudinal profile.

With the S. E. T. F. construction, the sheet iron will simply assume its original form, lengthwise corrugations and transversal depressions. The lengthwise undulations particularly are exactly and easily reformed as the S. E. T. F. by a happy structural design, has provided in each hollow of the corrugations one or more wire hoops placed lengthwise (Fig. 1) and these wires press on the sheet iron particularly at the proper time when the hollows must reform.

Another problem, the solution of which required great technical effort, is the construction of the neck and head for cylinders with very thin walls.

It is in fact very difficult to make a neck and a bottom with diameters of 170 mm., and with thicknesses of 1.5 to 1.6 mm. for instance. These two problems are actually solved; we have been manufacturing by the hundreds, seamless cylinders with two necks without any welding or with one neck and one closed bottom. In the latter case there is only one welded point 3 mm. in diameter in the center of the spherical cap forming the bottom on the opposite side of the head; this welding has no other purpose than to make the container gas tight and can be replaced by a threaded plug if one wants to avoid it.

Criticisms have been made of this method of construction.

The objection has been raised that due to the small thickness of the shell, oxidation will rapidly pierce it and make the whole equipment useless. We had foreseen this objection, which is well founded, by chromium coating the tube internally and externally. Experiments were made which show that a dull chromium plating, easy to apply, constitutes a powerful protection against rust; we have also successfully applied the protection of the Parker process.

The question of the lack of protection of the outside wires was also brought up; this question has also been solved.

Very serious accidents were predicted if one of the wire hoops gave way. This criticism is without foundation as the wires work under a very high coefficient of safety. Moreover if one of them breaks this will be noticed at once and the container can be repaired; besides the broken wire would be practically wedged in and held in place by the adjacent wires.

Finally if the metallic shell gave way, the wire hoops would prevent the scattering of the fragments of the interior envelope. The ballastic effects of such a scattering are dangerous with walls made of thick steel or semi-hard steel.

The value of the S. E. T. F. containers for the transportation of oxygen compared with the older processes of storage, is shown by the following comparison:

	<i>Wire Wound Receivers</i>	<i>Ordinary Receivers</i>
Weight of the 7,500-liter receiver at a pressure of 150 kgm., empty.....	38 kgm.	77.1 kgm.
Number of empty receivers per ton...	28	13
Weight of the 7,500-liter receiver at a pressure of 150 kgm., full of oxygen.	48.725 kgm.	87.825 kgm.
Number of full receivers per ton.....	20	11
Available volume of gas per ton transported.....	150 cu. meters	83 cu. meters

No comments are necessary after examination of this table. It is easy to deduce the savings in transportation coming from the adoption of wire wound cylinders.

If by means of wire wound cylinders a more complete advantage is taken of the process of storing the gases at 200 kgm. of pressure or more instead of 150 kgm., the above conditions are still more noticeably improved while preserving a high margin of safety.

On the other hand if the advantage of weights is partially waived the cylinders can be wired more heavily and be given a resistance which permits them to withstand considerably greater internal pressures.

The metal used to construct the gas tight wall has the following characteristics:

Mean resistance.....	40 kgm. per sq. mm.
Expansion.....	24 per cent
Elastic limit.....	20 to 23 kgm.
Resilience.....	25 kgm. per sq. cm.

As for the wire hoops they must meet the following conditions:

Resistance to rupture..	varying between 200 and 240 kgm. per sq. mm.
Expansion.....	1.6 to 2 per cent.
Elastic limit.....	190 kgm.

A wire fulfilling these conditions is used at the following stresses which assure a large coefficient of safety.

Unit stress—at experimental pressure.....	160 kgm. per sq. cm.
Unit stress—at working pressure.....	80 kgm.

*B. Special Containers for the Transportation of Gases in the Liquefied State.*<sup>2</sup> The idea of transporting liquefied gases is not new, but until now this method of packing was not sufficiently worked out to justify its industrial development.

The Dewar flasks stop to a certain extent the retransformation of the liquefied gases to their original state; they are used with success when dealing with small volumes and are accepted for rail transportation by the Berne Convention. The preservation of the liquefied gases being made as complete as possible under this form by modern processes, it is easily understood how advantageous it is to make use of them. Therefore if we consider the weight of one liter of oxygen in the gaseous form as 1.43 grams and that of a similar volume in the liquid state, as 1.118 kgm. and if we take into consideration the ratio of the weights under these two states, the liquid gives 851 grams of oxygen or 773 liters in the gaseous state.

One can see therefore what advantage can be taken of this contraction.

This question did not escape certain German technicians, especially Dr. Heylandt who specialized in the construction of apparatus for the production of oxygen through the liquefaction of air, and who developed a process for the transportation of liquefied oxygen and for its transfer into metallic receptacles at the points of arrival to facilitate its use under pressure for welding or cutting torches.

The author had proved experimentally that the transportation of liquefied oxygen would be of interest whenever it is possible to use containers of at least 500 liters capacity and weighing about 300 kgm. As this type of container holds 469 cubic meters of oxygen brought back to the gaseous state, the dead weight per cubic meter reaches only 0.639 kgm. instead of 10 to 12 kgm. with ordinary containers and of 5 kgm. with wire wound cylinders. If larger containers are used, the weight of 639 grams is reduced by more than half; a container holding 3,000 cubic meters brought back to the gaseous state weighs only 1,000 kgm.

A flat car on a standard gauge road provided with a tank of 4,500 kgm. capacity would transport 11,500 cubic meters weighing 15,500 kgm. To transport under the same conditions the equivalent of a

<sup>2</sup> U. S. Patent No. 1,680,873 of August 14, 1928.

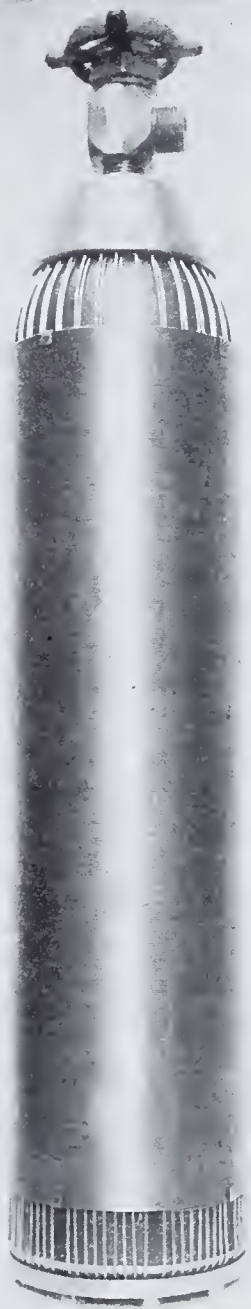


FIG. 3

tank car packed into ordinary cylinders of 6 cubic meters, 1,916 cylinders would be required weighing altogether 162,800 kgm. and would require more than 8 cars of 20 tons.

In wire wound cylinders this tonnage would be reduced by more than half.

The loss in weight during 24 hours for containers of at least 500 liters capacity would not reach beyond 2 per cent. As the German Government gave the necessary authorizations for the transportations of these containers by rail, customers are served when located at more than 350 kilometers by rail and at 200 kilometers by truck, the oxygen being produced very economically in a central plant with a large production.

Since 1920, at which date the original German patents were filed, the construction of receivers for the transportation of liquefied gases has made some progress and actually, thanks to the application of the new processes of the S. E. T. F., it is possible to completely eliminate the losses of gas during transportation.

On the other hand if, instead of transferring the liquefied gases by placing a given weight of liquid in a cylinder of known volume in order that the compression may take place progressively, these gases are led into gasholders, a source of difficulties will be eliminated.

It is in this way that the problem will present itself every time it is de-

sired to transport a gas with a high heat value to enrich a poorer gas held in a gasholder.

The Wire Wound Cylinder Company is therefore exploiting a process which completely eliminates the loss of liquefied gas transported and which reduces the cost of transportation equipment.

The containers built according to this patent, which was granted in all the principal countries, are of a particularly simple construction, since, contrary to what exists in containers of the Dewar type, there is no vacuum between the two walls.

An inner envelope, non-athermanous, in permanent communication with the atmosphere, contains the liquefied or solidified gas which is to be shipped. This first envelope is surrounded at a certain distance by a second athermanous vessel in such a way that there is between the envelope forming the reservoir and the athermanous shell a zone of circulation which is also at atmospheric pressure.

The bottom of the exterior athermanous envelope has a little reservoir which contains a liquefied gas which will evaporate in the annular space during the transportation, for instance a reservoir of liquid air. The annular space is moreover filled with glass wool or steel wool to the exclusion of all other materials, such as wool or cotton batting, kapok, etc., which are hygroscopic and consequently putrescible. The dead air, that is the air between the two walls has a conductivity of 0.04, mineral wool which has been used with success in the construction of insulated walls, has a conductivity of 0.05, much lower than plaster, baked clay, glass, etc.

If a small quantity of liquid air or nitrogen is stored in the small reservoir, the evaporation of these liquids going back gradually to the gaseous state will maintain the liquefied gas at a constant temperature and this will be so as long as the reserve of liquid air or liquid nitrogen is not entirely evaporated. It will therefore be possible to transport liquefied or solidified methane under the same conditions of time as if liquid nitrogen or liquid air were transported.

Since these shipping containers are in a fixed position on a truck or on a railroad car, it is therefore quite easy to carry the insulation to such a point that the losses are as small as possible and that for a given distance to cover, the expense in liquid air or nitrogen, auxiliary vehicles of low temperature, is lowered as far as it is possible to do so.

Methane has its liquefaction point at  $-164^{\circ}\text{C}$ . and its solidification point at  $-186^{\circ}\text{C}$ . It is best to place in the little reservoir some

liquid air which boils at  $-194^{\circ}\text{C}$ . and has a heat of vaporization of 125 calories while that of nitrogen is only 48 calories.

It is evidently impossible to transport in the liquid state gases containing hydrogen and compound gases such as illuminating gas or coke oven gases; on the other hand this method of transportation can be used perfectly well not only for methane, but also for ethane, propane, butane, ethylene, etc.—as well as for all other cracking gases with a high heat value; the construction of the shipping containers for these various gases will be the easier the higher their boiling point.

For methane the calculations show that a liter of liquid corresponds to a volume of 654 liters when brought back to the gaseous state.

One can see therefore what advantage can be taken from the economical viewpoint of the transportation of methane in the liquid state, although under this form this gas is less advantageous than oxygen from the fact of its lower density.

Assuming that the heat of vaporization of liquid methane is 51 calories and that there is a loss of 5 per cent every 24 hours instead of 2 per cent as the German author indicates it, from a tank car containing about 1,000 kgm. there will be lost 50 kgm. corresponding to  $50 \times 51$  or 2,550 calories or in round figures 3,000 calories.

Liquid air having a heat of vaporization of 125 calories, a reserve of  $3,000/25$  or 24 kgm. of liquid air will be needed which is not excessive, as, admitting that the price of this liquid air is 2 francs per kilogram, it can at once be seen that with an expense of 48 francs we can save more than 70 cubic meters of methane.

The operation is therefore justifiable from an economic point of view.

The containers being at atmospheric pressure there is no danger of explosion; in case of collision the methane would evaporate spontaneously and would be much less dangerous than a tank car of gasoline leaking or breaking open from a shock.

However, for rail transportation, the outlets of the inside reservoir should be vented and protected from burning cinders or other ignited materials.

It is perfectly feasible to transport into Paris by using this process, liquid methane coming from the coal mines of the Nord, manufacturing synthetic ammonia. As the maximum distance to be covered is 250 kilometers this distance can be made by special truck in 6 hours or by train during one night by the shuttling of cars constructed for that purpose.

It is therefore possible to provide Paris with methane in this form under more economical conditions than by putting the gas in ordinary cylinders or wire wound cylinders and that without any danger and without any appreciable loss.

It is very simple to build a 5-ton automobile truck chassis to transport 5,000 cubic meters when brought back to the gaseous state as well as to build a flat car.

For distances of 200 to 250 kilometers which are of the order of that from Paris to the various coal mining centers of the Nord and of Pas-de-Calais, the advantage remains first with liquefied gases, then with the transportation in wire wound cylinders.

As the construction of the means of transportation of gases in the liquid state, according to the patents of the S. E. T. F., presents no difficulty, this process brings an interesting solution to the problem of substitute fuels and a source of profit to the gas manufacturers.

Moreover the transportation of gases with a high heat value in large quantities and under the same liquid form makes it practical to recolorize all industrial gases under excellent conditions.

#### COST OF LIQUEFACTION

The transportation of gases in the liquid state is therefore possible in practice although one may suppose a priori that the cost of liquefaction is prohibitive.

It is easy to meet this objection.

For methane coming from the manufacture of hydrogen starting with coke oven gases, it is obtained directly in the liquid state; the objection therefore does not hold. It should, however, be mentioned that if liquid methane is taken from the columns, they are deprived of a reservoir of cold which may necessitate a modification of their construction. If a Linde or similar installation is used, making it possible to obtain directly a mixture of hydrogen starting with coke oven gases and of nitrogen extracted from atmospheric air, it seems that the enormous reservoir of cold of liquid nitrogen made available in that apparatus will permit extracting without any inconvenience the residual liquefied gases of which methane is the principal component.

If methane extracted from illuminating gas is treated to the limit to lower its heat value to 4,500 calories by absorption in activated carbon or by catalysis, or if methane is obtained by a biological process as acetone is obtained, it will be necessary in order to trans-

port it (*a*) either to compress it to 200 kgm. in wire wound cylinders, or (*b*) to liquefy it and put it in receivers without any pressure. But the work necessary for the compression to 200 kgm. is very close to that required for the liquefaction; solutions *a* and *b* are therefore practically equivalent as to consumption of energy.

As far as the loss due to evaporation during transportation is concerned it will always be less in a container of large capacity thus constructed for the transportation of liquefied gas. This gas, due to its great contraction in volume and to the reservoir of cold that it represents, can easily be protected and will take care of itself without any special cares and without any notable loss.

### CONCLUSIONS

The combination of the storing of combustible gases in wire wound cylinders under high pressure and of their transportation in the liquid state brings out various possibilities concerning the provisioning, stocking and refueling of motor vehicles.

These two processes meet all cases in common practice and make possible the long distance transportation of all industrial or mineral gases.

The rational development of these means of transportation opens a new avenue to the technique of the utilization of combustible or non-combustible gases by concentrating the manufacture and the preparation of these gases for shipment in central plants with a large capacity. The possibility of storing residual gases and of shipping them economically will lead to a lowering of the cost price of the main product and thus increase the margin of profit.

## A SUMMARY OF TESTS IN AUTOMOBILE FUELS

By A. GUISELIN

*Secrétaire General, Commission Internationale Petrole, Paris*

Among the important events which have taken place during the year 1928, in the realm of fuel substitutes for petroleum distillates, has been the third series of tests of automobile fuels (III Rallye des Carburants Nationaux).

These tests, organized by the Technical Commission of the Automobile Club of France, have received, for the past three years, material and moral assistance from Ministry Departments interested in the question of fuels; either as collectors of taxes, such as the Department of Commerce and Finance, or as representatives of the general interests of agricultural, maritime and land holding consumers, such as the Departments of Agriculture, War, Navy, and Public Works.

These trials included, besides the official departments mentioned and the Department of Inventions, large industrial groups, associated under various titles. Under the general title of "Contingent Producers" of fuels, we have the Colliery Committee, the Gas Society of Paris and the Syndical Chamber of the Petroleum Industry—the last-mentioned as importer of products for which substitutes are being sought.

This year, 1928, the number of entries was greater, due to the route selected which brought the tests into the territory of Belgium and Luxembourg. Thus we saw represented in these trials the automobile clubs of these countries as well as certain technical ministries.

These trials, as well as the previous ones, had no other scope than to gather, on the road, a certain number of vehicles propelled by energy derived from combustibles, which were to be, as far as possible, national, plentiful and economical.

This was done in order to show that we have a number of these fuels which when properly used and under certain special economic conditions, can satisfactorily replace petroleum now obtained from foreign countries at great cost. This cost reacts unfavorably upon our exchange and the general economic condition of the country.

A rule which fixes the course and the quality of the fuel allowed in these endurance tests, permits, besides a mixture of 50 per cent of

gasoline, the use of gasoline only as an auxiliary aid, limiting however, the capacity of the auxiliary storage tanks.

These auxiliary tanks must have a maximum capacity of 5 liters for trucks of 3 tons or over, net weight, and 3 liters for other trucks and pleasure vehicles.

## I. GENERAL CONSIDERATIONS ON FUTURE LESSONS WHICH WE MAY EXPECT FROM THE TESTS OF NATIONAL FUELS

The tests of national fuels have once again shown the flexibility of motors, which for the past 30 years, have been especially constructed to utilize thermal pressure of combustible gaseous masses, obtained primarily by mixing air with hydrocarbon vapors and, more recently, by moist vapor made up of liquid particles, more or less fine, produced in apparatus still called carburetors. This apparatus was named thus, assuredly, in remembrance of the first gasoline vaporizers which aided the automobile engineers of the last century to substitute for combustible illuminating city gas, mixtures of air more or less saturated with petroleum distillates (petroleum spirits), then alcohol vapors, benzol vapors and finally an infinity of combustible liquids incapable however, of competing with petroleum spirits, such as are obtained (now manufactured) from natural petroleum oils.

Oil fields have always revealed their presence at the opportune moment. That is, at the very instant when the consuming world was on the eve of resorting to energetic solutions of mixtures to which as early as 1917 we gave the name of national fuels. This historical date marked the advent of the scientific and at the same time mysterious technique of producing substitute fuels for petroleum spirits.

## II. SOLID FUELS

Two ways of utilizing solid carbon have been shown at the third series of trials.

I. The first consists in producing incomplete carbonization of carbon in small gas generators that are portable and sufficiently small to be placed, without too great inconvenience, on automobiles of present design.

II. The second consists in manufacturing gases from industrial carbonization of mineral coal and its substitutes and storing them in the most convenient way in containers as light as possible.

*Gas Producers*

*Agglomerated Fuels.* In order that gas producers be not too bulky and, at the same time, capable of producing large quantities of gas, either during a normal or an abnormal period (grade climbing), they must be fed with easily combustible fuels such for example, as wood charcoal.

It is this property which has been given the name of "reactivity" and which we have tried first to identify, then to measure from the time this mode of utilization of gas producers made its appearance.

This property has led us to seek the utilization of other fuels, if not more abundant at least more easily obtainable throughout France, than wood charcoal produced primarily in wooded sections.

These endeavors have been greatly encouraged by the first tests made on wastes of industrial wood charcoal by MM. Goutal and Hennebutte, originators of a process which furnishes small fuel briquets that are strongly agglomerated, resistant to shocks and humidity and burn very regularly from the exterior towards the interior without breaking into fragments under the influence of a current of dry or moist air or variable speed. These briquets are produced on an industrial basis, but at prices that are still too high.

Numerous tests have been successful with this new fuel, and have placed it among gas producer fuels now in industrial use.

A truck driven by a De Dion Bouton motor, fed by a producer called Rex, was entered in the Rally.

This truck, loaded with a dead weight of more than 10 tons, completed regular runs and once again has shown the worth of this artificial fuel.

Another truck, a Dewald-Peugeot, likewise equipped with a carbonite producer called Rex, has confirmed former results as to the flexibility and power of motors built to consume gas that is poor in calories instead of petroleum distillates.

This heavy truck, loaded with ten tons of paving stones, succeeded, during the Rally, not only in surpassing its rated speed and attaining more than 75 kilometers per hour, but helped its road companions, thanks to the powerful equipment which it had and to its great tractive power.

By substituting more or less simple and powerful air condensers for the former complex purifying apparatus of gas producers, inventors have been enabled to produce briquets of combustible substances derived from coal, lignite and peat.

Mr. Charles Roux is the inventor of a process for the carbonization of peat previously divided into small balls no larger than hazelnuts, which he calls "granols."

With these granols, he was able to feed a gas producer of his own design and to make automobile motors function in numerous controlled trials. But recently he thought it advisable to modify his first conception regarding the rôle of peat as a fuel.

He recommends now the use of peat as a binder which permits the agglomeration, always in the form of granules, of wood dusts (sawdust) charcoal, lean coal, semi-coke of coal, lignites, and peat.

For the practical application of these carbonized mixtures after agglomeration, he has constructed portable gas producers which can easily be placed on elegant pleasure cars.

Among the autos which were on exhibition at the Forestry Exposition of Versailles there was a 40 hp. Renault and a 23 hp. Peugeot which took part in a good portion of the Third Rally, joining it at Mons, after having been exhibited at the Peat Congress.

The functioning of the motors of these two vehicles was very regular notwithstanding the imperfections of one of them whose adaptation to the test conditions had been somewhat improvised.

The motors absorbed perfectly the gases produced by these heterogeneous fuels to which Mr. Roux has given the chemico-commercial name of "Syntho-Carbone."

In reality, this fuel, whose composition must vary according to economic circumstances and which, as yet, has not been manufactured industrially, must, according to its inventor, still realize a phenomenon of equilibrium which is both technical and economical.

These advantages were developed by him at the Eighth Congress of Industrial Chemistry held at Strasbourg.

According to Mr. Roux, wood charcoal and semi-cokes which he needs to manufacture his granules of syntho-carbone, are sold, at from 100 to 400 francs per ton respectively.

At this rather unremunerative price, the manufacture of these two products does not develop very rapidly, which is to the detriment of the application of the gas producer to the automobile.

Mr. Roux proposes to pay 50 francs more than the market price for these fuels so as to encourage their production. This will not prevent him, by using a 50-50 mixture and by agglomerating them with peat, producing by the expenditure of 50 francs a mixed fuel which will cost him 350 francs, and which he could sell for 400, a

cheaper price than that of its competitive fuels, that is at a far better price than wood charcoal and of course better than the carbonite.

With this fuel, gases can be produced in sufficient quantity to feed a motor at the rate of 5 hp. per square decimeter of grate surface. Hence a motor, rated at from 15 to 20 hp., will require, in reality, a very small producer, which could be placed, without great inconvenience, on the finest pleasure cars.

In order to prove this conclusively, Mr. Roux equipped, for the Rally, his 23 hp. car, with one of his producers, concealed in a very effective nickel plated case, in perfect harmony with the body of the car.

With this system of agglomerated combustible, as well as with carbonite, the gas producer can be reloaded without producing an excessive amount of black dust, one of the most important objections voiced against the use of charcoal as a fuel for pleasure vehicles.

This objection could not be raised if charcoal, even very fragile, could be put on the market in the form of small packages weighing 2 or 3 kg., the wrapper being of paper sufficiently strong to resist handling incidental to transportation, sale and loading. These packages could be inserted, wrapper and all, into the generators.

During the trials, Mr. Roux was able to show that sulphur and ashes produced by mineral semi-cokes no longer constitute serious objections, thanks to the improved systems of purifying gas.

*Wood Charcoal.* Let us point out at this point that charcoal gas producers have fed, during the trial runs, a great number of trucks equipped with Panhard, Levassor, Renault, De Dion-Bouton and S. E. P. T. motors.

Charcoal, needless to say, behaved very well. It showed that by taking certain precautions, bearing especially on the supervision of the gas producers, filters, and loading, the use of this economical fuel was very advisable.

Charcoal, much more fragile than briquetted fuels and above all much more dusty, requires special handling; skill is easily acquired by drivers, especially if the owners of these vehicles succeed in interesting these valuable auxiliaries of automobile progress in the use of such fuel.<sup>1</sup>

Among the commercial cars, whose motors were fed by charcoal, figured the famous Bus *Panhard-Lavassor*, seen for several years in all congresses dealing with replacement fuels.

<sup>1</sup> Charcoal can be introduced into the producer by means of a hopper and special buckets eliminating all dust.

This bus, which has covered more than 8,000 km., was used to transport officials. Here again it ran cheerfully its 1,700 km. at speeds varying between 40 and 50 km. per hour, speeds sufficient for the supervision of the Rally.

I have personally made more than five or six complete trips on this bus not only in perfect comfort and absolute cleanliness but without being annoyed by the incidental reloading which had to be made on the way due to the length of the trip.

Not once did the motor fail, except one day when the coal, which had been loaded, had not been sufficiently broken lengthwise before starting. This oversight, small in itself, shows, however, the great importance which must be attached to adjustment and regularity of adjustment in the gas producers.

This regularity of adjustment must be observed especially in the case of very small and active producers, such as used in touring cars.

However this is not so necessary when dealing with commercial trucks.

*Use of Agglomerate Lignite in Producers.* One of the principal inconveniences which had been attributed to charcoal was that it gave up tars which fouled the strainers and acids which corroded them within a comparatively short time.

In fact it is this real difficulty which may have been of some use to the new technique of special fuels for gas producers, about which we can say that the list begins with wood charcoal and ends with lignites and semi-cokes of lignites.

Wood charcoal is considered a type of dry fuel which contains a minimum of ashes, is free from sulphur and is the most perfect except, perhaps, for its low strength and lightness which necessitates a great deal of space.

Lignite, on the other hand, is not only a type of bituminous fuel, ashy and sulphurous, but is deemed most unsatisfactory because of the tar it yields in the intermediary stages of the producer.

However, lignite agglomerated without pitch, of the German type "Union" was used in the Rally on two trucks equipped with "Aster" motors fed by special producers designed by the society S. A. G. A. M.

During the first days of the tests these producers developed a difficulty which, a priori, would not surprise anyone. That is, that the aforementioned briquets, manufactured for a totally different use, abused in the crushing process, in a producer jolted by road con-

ditions, yielded annoying residues which, collecting in the lower portion of the producer, often hampered its action.

This defect was remedied by more frequent stoking and by means of briquets of smaller diameter. This defect the society S. A. G. A. M. expects to remedy by manufacturing more solid briquets of smaller dimensions.

With these reservations, it was noticed that cinders did not present any great inconvenience, certainly not any more than sulphurous tars which not once succeeded in reaching the purifiers.

Solid dusts, on the contrary, accumulated in great quantities in a special receptacle, easily accessible and quickly cleaned.

The fact remains, however, that these producers, whether perfectly or not, did function and that the cars upon which they had been installed reached their destination each evening within the time allowed by the rules of the tests.

Let us remember that these producers, designed to burn wood, consist primarily of an open cylindrical and vertical container whose lower portion is equipped with a double jacket filled with refractory substance heated red hot by the zone of combustion.

The air necessary for combustion enters by means of two circular rows of blast pipes, placed above and below the zone of combustion.

The gas, after having been changed into a mixture of nitrogen and carbon monoxide, probably containing tars, is led into the circular jackets with a small amount of secondary air which produces a partial combustion of the carbon monoxide in the pile of refractory material where the tars are completely burnt or decomposed.

Hence it is a perfectly combustible, gaseous mixture which leaves the generator and reaches the motor.

*Combustible Gases.* Now let us examine the new way of utilizing carbon of combustibles.

This new method consists in transforming these carbons into gas by carbonization at high or low temperatures and then placing these gases on vehicles in tanks suitably designed to comply with the limitation of weight and space allowed for pleasure cars and trucks.

Although, in certain cases, it is not impossible to store gases, at atmospheric pressure, in tanks necessarily bulky, the current practice of this method of carburization of motors, has led to the choice of steel tanks, similar to those used to transport oxygen, carbonic acid, and hydrogen either compressed or liquefied.

These containers are generally constructed according to certain

rules which show that the dead weight of these flasks becomes constant beyond certain pressures.

Space is evidently one of the interesting factors of this problem of utilization of gases but we cannot overlook the weight of the containers. It is for this reason that certain engineers have set aside the laws of resistance of metals, by substituting for pressed steel pipes, containers of thin metal, very ductile, reenforced with a double longitudinal and transversal hoop made of steel wires (similar to those used in pianos) and easily resisting tensile stresses of 250 kgm. per square millimeter. They are thus capable of diminishing considerably the weight of the containers, bringing it down, for example, from 10 to 11 kg. per cubic meter of gas stored at 1 kg. of pressure to 5 or 6 kg. and even 3 kg. in the case of gases cooled to very low temperatures.

The enumeration of the advantages of this system of storing combustible gases and especially methane, which can be compressed much more than Mariotte's Law would allow, will be the object of a special communication at the Second International Congress of Pittsburgh. We will not dwell longer on the technical side which this question presents.

We will mention only that numerous studies have been undertaken in France during the past two years, aiming to extend the application of the method of feeding city gas and coke-oven gas to motors, for the organization of public transportation as a whole or for large industrial transportation.

The most recent use of combustible gas flasks was made by the Petroliferous Research Society of Vaux en Burgey, where the sources of natural gas, known for several years, were in 1923 and 1924 the object of systematic exploitation. However, the sudden exhaustion of these natural supplies, unfortunately, wrecked many hopes. Nevertheless during this brief period a whole system of transportation vehicles, fed by natural gas, was put forth which gave impetus to the present trend as found in the 3d series of tests.

It is because the United States possess famous deposits of natural gas rich in methane, deposits as yet badly exploited, that we are desirous of pointing out to the Pittsburgh Congress the interest which a general application of these methods might present to this great country especially since they apply to gases of high caloric power and very compressible.

Natural gases, even when first freed of their hydrocarbon liquids at ordinary temperatures, have a residual caloric power that is very

high and is surpassed only by rich gases obtained by cracking heavy oils or by carbonizing bituminous coal at low temperatures.

Notwithstanding the fact that France does not possess important natural gas deposits, nevertheless it must face the problem of making use of all its plants producing artificial gases, first in the city gas plants, then in cokeries and finally, in the future, in plants carbonizing at high or low temperatures or engaged in cracking heavy oils.

It is with this practical aim in view that serious researches have been undertaken by MM. Chapuis and Pignot, under the auspices of the Gas Society of Paris, with a view to determining the limiting proportions of oxygen or air, which can exist in coal gas without the pressure of 200 kg. presenting dangers of explosion, dangers which for a long time have handicapped these industrial gases.

At the present time these limits are extremely large and, by taking measures already known, we may say that these compressed city gases can be used by careful consumers without any danger.

Such conclusion, therefore, induced the Society for Public Transportation in the Paris district to enter in the Third Rally, two auto buses of standard model, each equipped with six ordinary steel containers of standard type and having a capacity equal to 23 liters. This capacity is sufficient to store a quantity of gas compressed at 150 to 200 kg. necessary for the daily runs of these buses.

These two buses, besides their customary gasoline carburetors, were equipped with pressure regulators and mixers type VAUX to which was added, on the way, additional air regulated at will by a hand lever easily accessible to the driver and replacing the ordinary carburetor. These two trucks, within the speed conditions, accompanied these competing in the Rally and received, on the way, their supply of compressed gas from the gas plants of the towns through which they passed.

Moreover, they were serviced daily, at their destination, by a compressing station made up of:

1. A  $2\frac{1}{2}$  ton Panhard-Levassor tractor truck driven by compressed gas stored in 8 tubes of 7 cubic meters placed under the body of the truck and having, in the cradle, 4 rows of 7 tubes to be used as emergency supply for the competing buses.

2. A towing truck, a real miniature compressing plant, consisting of a three stages Spiros Compressor type M.V. 150, capable of compressing gas to 175 kg. with an hourly flow of 22 cubic meters, and a compressor called "Super Compressor" Spiros, to be used to com-

press the residual gas of the flasks emptied, that is, capable of taking in at once gas already compressed.

This "super-compressor" acting as the 4th phase of a stage compressor is of the ACF monocylinder type with a flow of 22 cubic meters, the gas admitted being taken at pressures varying between 80 and 25 kg.

On this little portable plant, the compressor itself is actuated by a belt from a 4 cylinder 12 to 15 hp. C.L. motor, while the supercompressor requires only a 3 hp. C.L. monocylinder motor.

The cooling of the gases is assured by a supply of water that is constantly cooled by means of a radiator having a very large surface.

3. Finally, a battery of 18 tubes of 40 liters capacity, equipped with feeds and stopcocks to insure filling and discharging under like conditions, completes this equipment which will be put, after the tests, at the disposal of groups interested in the diffusion of compressed air traction and desirous of pursuing further researches.

For this purpose, the trailer has also a small gas testing laboratory and a small De Dion dynamo which supplies light and heat for an apparatus called a deoxygenator.

All these experiments have shown that gas can be substituted for gasoline in motors now used in driving French trucks or buses.

It is evident that the hypothesis made on the return price of these calories, which could be obtained at half the price of those of gasoline, opens a very interesting future for this application, taking in consideration, however, the high duty placed upon gasoline and which has as yet not affected replacement fuels such as gas, wood charcoal, and the various agglomerates we mentioned in the preceding chapter.

### III. A NEW WAY OF UTILIZING HEAVY OILS

If we consider that the trials, according to the idea of their organizer, Colonel Ferrus, had for their purpose not only the substitution of national products for foreign fuels but also to seek a practical method of reducing the price of fuels used, we must devote some attention to the experiments tried with a view of substituting a motor burning cheaper oils for the present gasoline motor.

This solution was shown in the third series of tests by the Motor Company of Lille which entered two vehicles, a truck and a bus, driven by motors using heavy oils. These engines were modified Diesels.

The Peugeot Junkers Motor, which will now be described, is in every respect a heavy oil motor and in no respect a modified gasoline motor.

This motor consists essentially of a vertical cylinder open at both extremities and within which move simultaneously, but in opposite directions—from the extremities toward the middle and inversely—two pistons attached to a crankshaft by means of rods keyed on at  $180^\circ$  apart.

When these pistons, coming close together, have sufficiently compressed the air which has been pressed into the cylinder on the preceding stroke, a pump injects into this center portion of the cylinder a certain quantity of oil which at once ignites.

The two pistons are then pushed back and at the end of its stroke the lower piston opens exhaust vents cut into the walls of the cylinder; other vents in the upper portion are also opened by the upper piston and admit a violent current of fresh air which expells the burnt gases.

The pistons then return to one another to compress the fresh air that has just been admitted, heat it to a point sufficiently high to ignite the atomized combustible admitted at a set time.

The cleaning air is produced during the combustion stroke by a very large piston surmounting the upper cylinder, which forms a slide block and displaces itself in a cylindrical position at the head of the frame containing the motive parts.

The fuel is mechanically compressed by a special plunger pump set in motion by the crank shaft.

One can easily see the advantages of such an arrangement which does away with valves, ignition, inertia and explosion strains while perfectly filling the cylinder with air and ejecting all the burnt gases.

In fact, a motor consisting of one cylinder with a bore of 60 cm., stroke of  $90 - 120 = 210$  cm., at a speed of 1000 revolutions yields 8 hp. with an average consumption of 210 grams of heavy oil per horsepower. An amount which is quite acceptable. Its weight is 200 kg., hardly 25 kg. per hp.

The bus equipped with a motor of this type but having two cylinders, functioned during the trials very regularly and with good pickup. It would indeed be interesting to know the mechanical results of this trial for a distance of 1,500 kg. and to examine the cylinders, the pistons, the segments, and the valves.

This is a very interesting solution of the problem of using heavy oils on industrial and pleasure vehicles. Especially if it can be

applied to heavy oils derived from tars obtained from the distillation at high or low temperature of coal and lignites.

This solution, in fact, falls in the realm of those which strive to discover the utilization of national and cheap liquid fuels.

It is for this reason that we wish to call this subject to the attention of the bituminous coal congress at Pittsburgh where the question of the direct utilization of coal tars is bound to come up.

It is quite evident that at the present time it is preferable to find a good motor burning coal oils directly rather than to seek the means of transforming these tars with costly hydrogen in order not to burn them any better in a gasoline motor.

*Light Liquid Substitute Fuels.* In order fully to cover the field, we must mention that in the Rally were included certain vehicles whose motors were fed by benzol with mixtures of alcohol and gasoline, with fuels extracted by special treatment applied to heavy petroleum and coal oils, as well as synthetic fuels, such as methyl alcohol.

These motors behaved very well and their presence in the trials confirmed what we knew about them.

We shall add nothing more except that these fuels produced more reasonably, cannot be sure of success except in so far as they are the by-products of an important and necessary industry such as that of carbonization.

Benzol meets these conditions; the same is not true of methyl alcohol when it is derived from methane which can be burned directly or when it is derived from a mixture of carbon monoxide and hydrogen, when this mixture is nothing but a transformation of coke which can also be used to feed auto producers.

This, however, is not true of ethyl alcohol, an agricultural product coming primarily from the fermentation of beet sugar, because beets are necessary for feeding animals and their cultivation is considered complementary to that of wheat and cereals.

In conclusion, we predict the speedy end of liquid synthetic fuels and the success of methods which dealt, before the application of producer gas, with the use of coal carbon in its most direct form, thus eliminating losses in transportation and useless and costly transformations.

Let us hope that this conclusion may inspire those attending the Second Congress on Bituminous Coal of Pittsburgh.

## CONCLUSIONS

As to the conclusions to be drawn from the third series of tests we may say the following;

We witnessed, in the third series of trials, the disappearance of certain fuels and the advent of others more or less synthetic or catalytic, while the success predicted in favor of feeding motors with gas produced by compact gas generators, has more than fulfilled all expectations.

In fact we have seen a new-comer: gas manufactured in industrial apparatus and stored in tanks whose weight has been decreased by ingenious methods.

We wonder whether it is wise to risk much capital in large synthetic plants, when we can imagine coal, after carbonization, being used directly as a fuel, thanks to the producer, while its gas could be stored in flasks and used as fuel for touring cars.

The results of our investigation have finally led us to the simplest conceptions, that is, of burning primary fuels directly in motors, thus doing away with the expenditure of immense sums to convert them into gasoline.

It is for this reason, that we ought to compliment ourselves upon this result, since it puts into the hands of industrial nations the end of bitter competition which many imagine will be the cause of future wars.

Has it not been said that petroleum is so indispensable to the life of nations that its possession would bring about wars between friendly nations?

No congress could be better designated to receive these pacifist ideas than the one to which this report is addressed, since it has been organized by an institution endowed by a man who has done so much for peace.

It is quite evident that this great benefactor must have inspired the author of these lines.

The author offers him his sincerest thanks from the bottom of his heart—the heart of a Frenchman who has lived the horrors of a cruel and merciless war in which petroleum contributed its share to the victory of the Allies since it was used to burn alive thousands of helpless soldiers.

## SUPPLEMENT OF REPORT ON THE THIRD RALLY OF NATIONAL FUELS

*A New Orientation to Fuel Researches*

Last September there was organized, in the north of France, a competition for auto vehicles, called "paved road vehicles" because the distance to be covered by them consisted primarily of paved roads, a fact which increased the difficulty of the trip.

This contest imposed severe conditions upon the commercial-vehicles section. A cup was to be awarded to the truck which, having kept up the assigned speed and having reached its assigned stopping places, in the allotted time, showed that it had consumed the least amount of fuel per kilometer.<sup>2</sup>

An Aries truck equipped with a generator S. A. G. A. M., using lignite briquets which we noticed especially in the Rally of National Fuels (our report of September, 1928), took part in this contest and competed with trucks using heavy oils, acetylene, and charcoal, that is, fuels other than the cheapest gasoline.

The grates of the generator S. A. G. A. M., had been somewhat modified to allow the direct use of unbroken lignite briquets. (The breaking of the briquets and the formation of dusts had been the chief objections against this fuel during the Third Rally.)

The result of this new trial was that the 4-ton Aries truck, loaded at the start with 5 tons 600 kg. dead weight, was able to transport almost 10 tons in three days over a distance of 600 km. of paved roads, with a consumption of 538 kg. of lignite briquets which re-tailed in Lille at 200 francs per ton.

This consumption corresponds to an expenditure, in francs, of 0.0185 per kilometric ton, while contestants classed next in order attained 0.0879 and 0.1198.

It must be noted that in this group of vehicles there were trucks equipped with "Dewald" generators especially designed to use charcoal, and gasoline trucks of the Liberty Willeme Chenard, Wlker., model.

The following are the results of the contest.

First Prize No. 4 Aries Truck (unbroken lignite briquets):

Total load, 9520 kg.

Distance covered, 610 km.

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<sup>2</sup> These tests were controlled officially and strictly. Controllers were installed on all vehicles and during the night the vehicles were watched by the police.

Fuel used, 535 kgm. at 0.20 c. per kilogram.

Price per kilometric ton, 0.0185.

Second Prize No. 20 Peugeot Truck (acetylene and heavy oil):

Total load, 2862 kg.

Distance covered, 610 km.

Fuel used, 83 liters at 1 f. 85 per liter.

Cost per kilometric ton, 0 fr. 0879

Third Prize No. 29 Rochet Schneider Truck (heavy oils).

Total load, 2840 kg.

Distance covered, 610 km.

Fuel used, 194 liters at 7 fr. 07.

Cost per kilometric ton, 0.1198.

It must be noted that the Aries truck, due to slight road accidents, such as broken magneto springs, a broken ceupin and a broken gas pipe was penalized 53 points which represents a delay of 106 minutes over trucks using gasoline.

In order to be consistent with the conclusions presented to the Second Congress at Pittsburgh, we restate that what interests us most in these results is not so much the cost of this fuel, 1.8 centimes per kilometric ton, that is  $\frac{1}{20}$  cent, as the perfect functioning of the motor over a distance of 600 km. completed in 3 runs of 200 km. per day.

Therefore, with a solid fuel, very much objected to as a combustible for generators, it was possible to drive an overloaded truck over rough roads for a distance of 600 km. at an average speed of 20 km. per hour.

Here we have a manifest proof of the uselessness of converting, at great cost, this lignite into liquid fuel.

This allows us to suppose that the only worth-while researches are those aiming at the manufacture of cokes, beginning with coal sufficiently reactive to be burnt in automobile generators.

It is possible that this conclusion may sadden the partisans of synthetic fuels, derived from coal, and that it may tend to ruin hopes based on colossal factories which have swallowed enormous capitals, but we need not be uneasy about these consequences, when we place ourselves on the side of assured economic realizations.

That is why we insist, once more, that this conclusion be presented to the Second Congress at Pittsburgh notwithstanding the opposition it may encounter.

## DISCUSSION

P. NICHOLLS (United States Bureau of Mines, Pittsburgh, Pa.): The advantages of the principles shown in the particular producer that Mr. Chapman illustrated, where that producer is of the size which is shown in the illustration and used for such purposes, were very clear.

But I would suggest that he was not quite so definite in supporting his vision that the same principles could be applied and are likely to be applied for large power units in the future.

As he pointed out, the line of demarcation between the producer principles he suggests and the stoker is not at all definite and I believe would tend to be more indefinite as the size increases.

As he showed, the size would be distinctly limited by the method of feed, and the central feed could not be extended beyond a certain diameter. In that case, it would mean that in order to apply it to large units, you would have to have a number of small units, which in itself would decrease the possibility of getting the advantages of constructional cost, due to the increased size of the installation.

The main difference in principle between that which he shows and the underfeed stoker I believe could be construed as being that in his method he has a way whereby he can supply secondary air under controllable conditions and can insure complete combustion, and probably complete combustion in a smaller volume than he could where the gases are not under so much control; in an underfeeder a larger volume and longer path of travel for the gases is required in order to insure combustion.

It is therefore questionable whether the saving in height the author estimates, as based on a small installation, would apply to a large installation because, apart from the increased height of the producers themselves, the larger throat diameter would require an increased height for combustion after the gases leave the producer.

I would like Mr. Chapman to give us a little bit better definition as to how the design would be carried to larger sizes.

A second question I would like to ask is: In a producer of the size he shows—or of that order—what would he aim at, in the percentage of gas producer action? Or expressed in other words, what percentage of his fuel would he propose to convert to carbon monoxide or hydrogen? Or what percentage of the total heat would he propose that the gases should have as sensible heat before they enter the throat where the secondary combustion occurs?

W. B. CHAPMAN (Consulting Engineer, New York): In answer to the question about the possible size of gas producers for heating boilers: I have operated underfeed gas producers from 1 foot to 10 feet in diameter and believe they could be built in sizes up to about fifteen feet in diameter. A producer 15 feet in diameter would have a fire bed area of 177 square feet which would gasify approximately 17,500 pounds of coal per hour which in turn would develop 5,000 h.p. figured at three and one-half pounds of coal per developed h.p. For the present I do not see any immediate market for sizes under 100 h.p. but believe that ultimately special equipment will be built for two-stage combustion in all sizes.

In reply to the question concerning the quality of gas that is made in the underfeed type of gas producer: This gas contains about 130 B.t.u. It averages about the same as gas made from anthracite coal, being richer than the gas made from coke but leaner than the gas made from bituminous coal. If the gas is to be used direct for firing boilers its richness is not particularly important. The thing that is important is dependable uniformity.

Answering the question about the thickness of the firebed: Three feet to four feet deep is about right for making good producer gas. If desired the thickness of the firebed might be gradually reduced until no secondary air at all was required, provided the mechanical agitation employed was not too severe for a comparatively thin firebed. However, if the firebed were maintained at the thinnest minimum, a very great advantage would be lost, for under such conditions the producer firebed would respond no better to a sudden overload than the ordinary mechanically stoked firebed. The overload could not be handled until the firebed could be thickened. It therefore would be best to keep the firebed always at the maximum thickness required for maximum capacity. It then would be ready to respond instantly to any amount of overload imposed. It is a peculiar fact about making producer gas that a firebed thick enough to gasify the fuel at the rate of 100 pounds per square foot per hour will make gas equally good, if not indeed better, when operating at the rate of 10 pounds per square foot per hour. Mechanically stoked firebeds for single-stage combustion have no such latitude of operation. In theory, at least, the advantages all lie with two-stage combustion.

GODFREY M. S. TAIT (Consulting Engineer, Washington, D. C.): I would like to ask Mr. Chapman if he ever made any comparison as to the percentage of ash which he can use in the fuel for his producer and what is the high limit on that substance.

It stands to reason that an ash of very much lower fusing temperature could be used in the producer because so much heat is removed by the steam in the blast.

I would like to know if he can make any statement on that

MR. CHAPMAN: There is no limit in the low-fusing point you can use, because it is the part of the steam to prevent the fire bed from getting too hot. When the fusing point of the ashes gets lower, you put in more steam and take care of it. You can handle any fuel no matter how bad it is. I have not personally handled anything less than 1800°F. melting point, but have had a great deal of that, and can handle it if it is necessary to put in something like 50 per cent steam of the weight of the coal, which would represent perhaps 5 per cent of the coal used up in making steam. But that cannot be considered as loss. So my answer would be, there is not any limit.

CHAIRMAN LANDIS: I suppose you are familiar with the fact that they go to the extent of melting the ash.

Is there any further discussion? As neither of the other authors are here, it is rather difficult to ask for discussion on the other two papers, but I think there might be some comments or remarks that you may wish to add, and if you have questions, we will see what we can do in the way of answering them.

The first paper is on, "Rational Utilization of Fuel Gases." Then there is the paper on automobile fuels. Surely we must have some automobile people here who are interested in that.

JEAN BING (Comité Central des Producteurs et Distillateurs du Doudron en France, Paris): I must say that Mr. Guiselin in expressing his views expresses the conclusions of many other French authorities and engineers.

It seems in particular that it will be always better to use a liquid fuel because they are more easily handled than solid fuels. The solid fuels can be used in case of emergency. For instance, we have no petrol, and it may happen that we have no connection with the oil fields at a certain time, because of blockade, or it may be impossible to buy liquid fuel from Europe.

CHAIRMAN LANDIS: I think I agree with that myself. I have seen some of those cars working abroad. They would not get very far if they got into traffic and the green light came on, because they have little or no acceleration. They get stalled.

Of course, you may have to do like we used to do with the old Ford tractor—get out and turn the gasoline tank on. They are not self-starting. We do not know what could be done in the way of acceleration.

Of course, most European motor car engines are rather low horsepower compared to ours. They are paying two or three or four times as much for gasoline, and they pay more attention to economy and less attention to rapid acceleration. But I think that can be helped by engineering. Certainly, as it stands today, they would not get very far on Fifth Avenue.

MR. NICHOLLS: Did the paper cover as to how long it took to start up one of these producer gas vehicles? It mentioned them as being applied to private vehicles as well as to public vehicles. The application to a truck or to a public vehicle would appear to be very much better than it would to a private vehicle where you wanted a short starting time for occasional use.

MR. BING: They use a particular one in private cars driven by chauffeurs, and it does not take a long time to start. But I must say that he may use either the gasoline or producer gas, because he can shift over to the carburetor. But when he wishes to start only with the producer gas, it does not take a long time, only about three or four minutes. If you order your car with the chauffeur, it will be ready. It does not take long. It will be ready for your use as soon as you order it. I do not think it is an impossibility.

MR. WILLIAM B. CHAPMAN: I would like to inquire to what extent if any they have experimented with mechanically-agitated firebeds in France for these special gas producers for automotive purposes in order to obtain a greater degree of reliability.

It seems to me that before the problem of using gas producers for automotive purposes is solved, we must have a reliable, mechanically operated producer for gasifying cheaper grades of solid fuels than the very special, high-priced fuels containing little or no ash to which we are at present limited. Although

it is true that even high-priced charcoal cuts the fuel cost in two, that is hardly enough to warrant one in going to the bother and the inconvenience of operating a gas producer. People in most countries—especially in this country—are willing to pay a great deal more for gasoline which may be classified as a fuel luxury rather than go to the bother of operating a producer.

I have experimented with an underfeed gas producer 14-inch inside diameter, for driving a truck. The fuel was No. 1 buckwheat anthracite costing less than one-fifth as much as gasoline per B.t.u. I have also built an experimental 18-inch diameter underfeed producer for gasifying Bituminous coal screenings costing less than half the price of Anthracite. The producer was mechanically agitated from beneath, the walls were of metal and air cooled. The Anthracite was quite easy to handle but the Bituminous slack caked rather badly in such a small producer. Small sizes of coke,  $\frac{1}{8}$ -inch to  $\frac{1}{2}$ -inch, would probably have worked as well as anthracite.

Our Anthracite mine operators might develop an all-the-year-round market for their fines if they were willing to do the preliminary pioneering necessary to show the trade what practical possibilities exist for the use of anthracite in the automotive field—particularly for trucks and tractors. The farmer who now pays \$5.00 a day for gasoline for his tractor would appreciate getting an equivalent amount of fuel for \$1.00.

We have forgotten the time when teamsters used to get up early in the morning, feed and curry their horses, then hitch them up before “starting” their day’s work. The hour a day formerly spent in caring for horses could be reduced to five or ten minutes a day caring for the gas producer. I believe farmers and truck drivers could be induced to spend that much time if the fuel used were four or five times cheaper than gasoline—not just half as expensive, as in the case with charcoal. It would require a mechanically operated producer 12 inches to 20 inches in diameter and I believe it could be accomplished with a little judicious experimenting.



CARNEGIE INSTITUTE OF TECHNOLOGY  
SCHENLEY PARK, PITTSBURGH

# PROGRAM OF THE SECOND INTERNATIONAL CONFERENCE ON BITUMINOUS COAL

LATEST DEVELOPMENTS IN UTILIZATION

*November 19 to 24, 1928*

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## MONDAY, NOVEMBER 19

REGISTRATION: Foyer of Carnegie Music Hall, 9:00 A.M.

MORNING SESSION—10:00, Carnegie Music Hall

### GENERAL SESSION

Chairman: President Thomas S. Baker

Addresses of Welcome

DR. THOMAS STOCKHAM BAKER, President, Carnegie Institute of Technology

T. P. GAYLORD, President, Chamber of Commerce of Pittsburgh

*The Work of the British Fuel Research Board, 1927 to 1928*

DR. CECIL H. LANDER, Director, Fuel Research Board, London

*Catalysis Applied to the Conversion of Hydrocarbons*

DR. CARL KRAUCH, Director, I.G. Farbenindustrie Aktiengesellschaft, Ludwigshafen am Rhein

Introduced by Walter C. Teagle, President, Standard Oil Company of New Jersey

Discussion and questions

AFTERNOON SESSIONS—2:30

### LOW TEMPERATURE DISTILLATION SECTION

Carnegie Music Hall

Chairman: J. D. A. Morrow

*The Economics of Low Temperature Coal Treatment*

W. A. DARRAH, President, Continental Industrial Engineers, Inc., Chicago

*Low Temperature Carbonization of Coal by the Hayes Process*

JAMES BALPH, Secretary, Coal Carbonization Company, Pittsburgh

M. J. McQUADE, President, Ben Franklin Coal Company of West Virginia, Pittsburgh

Discussion and questions

## ORIGIN, COMPOSITION AND CLASSIFICATION SECTION

Carnegie Lecture Hall

Chairman: C. A. Meissner

*General Considerations on the Origin and Nature of Bituminous Coals*

*The Nature and Properties of Siberian Bogheads*

DR. GEORGE L. STADNIKOFF, Karpow Institute of Chemistry, Moscow

*The Classification of North American Coals*

A. C. FIELDNER, Chairman, American Engineering Standards Sectional Committee on the Classification of Coal, and Chief Chemist, U. S. Bureau of Mines, Washington

Discussion

RALPH H. SWEETSER, American Rolling Mill Company, Columbus, Ohio

DR. GEO. H. ASHLEY, State Geologist, Harrisburg, Pennsylvania

DR. R. THIESSEN

## PULVERIZED FUEL SECTION

Carnegie Union, Carnegie Institute of Technology

Chairman: Geo. A. Orrok

*Internal Combustion Engine for Powdered Coal*

\*RUDOLPH PAWLIKOWSKI, General Manager, "Kosmos" Maschinenbauanstalt, Görlitz, Germany

Read by Professor Willibald Trinks, Carnegie Institute of Technology

*The Powdered Coal Locomotive of the Allgemeine Elektrizitäts Gesellschaft*

\*BAURAT WALTER KLEINOW, Hennigsdorf, Berlin

Read by Dr. Lionel Fleischmann of the A. E. G., Berlin

*Pulverized Fuel and Its Various Fields of Application*

\*DR. GEORGE E. K. BLYTHE, General Manager, The Buell Combustion Company, Ltd., London

Read by Professor T. G. Estep

Discussion and questions

## TUESDAY, NOVEMBER 20

MORNING SESSIONS—9:30

### GENERAL SESSION

Carnegie Music Hall

Chairman: Samuel Insull

*Contributions to Knowledge of the Transformation of Cellulose and Lignin into Coal*

DR. FRIEDRICH BERGIUS, Heidelberg, Germany

*The Low Temperature Distillation of Coal*

S. W. PARR, Professor of Applied Chemistry, University of Illinois, President, American Chemical Society

\*Indicates author is not present.

*Coal, Hydrogen and Capital*

F. ZÜR NEDDEN, Dipl.-Ing., Secretary, Fuel Committee of Reichskohlenrat, Berlin

Discussion and questions

## AFTERNOON SESSIONS—2:30

## LOW TEMPERATURE DISTILLATION SECTION

Carnegie Music Hall

Chairman: G. St. J. Perrott

*Modern Developments in Lignite Carbonization*

DR. F. P. KERSCHBAUM, Technical Advisor of Metallbank und Metallurgische Gesellschaft, Frankfurt, Germany

*The Low Temperature Carbonization Plant at the Imperial Research Institute*  
YOSHISADA BAN, Chemist, Imperial Fuel Research Institute, Tokio, Japan

*The Influence of Inorganic Materials in Lignite Carbonization*

A. W. GAUGER, Director, Division of Mines and Mining Experiments, University of North Dakota

\*DONOVAN J. SALLEY, University of North Dakota

*Notes on the Use of Smokeless Pulp Binders for Briquetting*

\*C. J. GOODWIN, Chartered Civil Engineer, London

\*G. N. WHITE, Consulting Technical Chemist, London

Read by Robert M. Crawford

Discussion and questions

## ORIGIN, COMPOSITION AND CLASSIFICATION SECTION

Carnegie Lecture Hall

Chairman: Charles E. Ferris

*The Rôle of Humic Acids in the Transformation through Heating of Coal and in the Production of Coke*

\*DR. ING. FRAN PODBREŽNIK, Belgrade

Read by Professor Thomas R. Alexander, Jr., Carnegie Institute of Technology

†*Phenolic Solubility of Humic Acids*

\*DR. ING. FRAN PODBREŽNIK

\*MARCEL SOUM

Read by Dr. T. R. Alexander, Jr., Carnegie Institute of Technology

*Relation between the Fossil Combustibles and the Gaseous Products Resulting from Their Destructive Distillation*

\*PROFESSOR PAUL LEBEAU, Faculté de Pharmacie de Paris, Paris

Read by Professor J. H. James, Carnegie Institute of Technology

*Recent Developments in Coal Research*

DR. REINHARDT THIESSEN, U. S. Bureau of Mines, Pittsburgh

Discussion and questions

\*Indicates author is not present.

†Read by title.

### PULVERIZED FUEL SECTION

Carnegie Union, Carnegie Institute of Technology

Chairman: H. E. Howe

*Thermodynamic Bases of Pulverized Coal Combustion*

DR. ING. P. ROSIN, Mining Academy of Freiberg, Germany

*Burning Bituminous Coals in Pulverized Form*

HENRY KREISINGER, Research Engineer, The Combustion Engineering Corporation, New York

*The Modern Stoker and Its Comparison with Pulverized Coal Firing*

JAMES W. ARMOUR, Vice President and Engineering Manager, Riley Stoker Company, Worcester, Massachusetts

Discussion and questions

### FERTILIZER SECTION

Faculty Club Room, Carnegie Institute of Technology

Chairman: Charles L. Parsons

*Economic Phases of the Fertilizer Industry*

C. H. MACDOWELL, President, The Armour Fertilizer Company, Chicago

*By-Product Nitrogen and the Fertilizer Industry*

CHARLES J. BRAND, Executive Secretary and Treasurer, The National Fertilizer Association, Washington

*The Combined Synthetic Ammonia and Coke Oven Plant of the Union Chimique Belge, at Ostend, Belgium*

F. A. F. PALLEMAERTS, Manager of Research, Division of Coke Ovens and Synthetic Ammonia, Union Chimique Belge

Discussion

C. J. RAMSBERG, Vice President, The Koppers Company, Pittsburgh

### PUBLIC EVENING SESSION

8:15, Carnegie Music Hall

Chairman: Emil Winter

*The Synthetic Kingdom*

DR. EDWIN E. SLOSSON, Director, Science Service, Inc., Washington

*The Technical Lessons of the World Power Conference, 1928*

DR. E. W. SMITH, Technical Director, Woodall-Duckham Companies, London

## WEDNESDAY, NOVEMBER 21

MORNING SESSIONS—9:30

### GENERAL SESSION

Carnegie Music Hall

Chairman: Frank B. Jewett

*Coal Consumption as Affected by Increased Efficiency and Other Factors*

\*DR. ARTHUR D. LITTLE, Consulting Engineer, Cambridge, Mass.

DR. ROBERT KLEINSCHMIDT, Physicist, Arthur D. Little, Inc., Cambridge, Mass.

\*Indicates author is not present.

*From Coal to Rubber*

DR. FRITZ HOFMANN, Schlesisches Kohlenforschungsinstitut der Kaiser Wilhelm Gesellschaft, Breslau

*Oxidation of Hydrocarbons*

E. PAUL DUMANOIS, Directeur des Services Techniques de l'Office National, Paris

Read by Jean Bing

Discussion and questions

## . PURIFICATION AND CLEANING SECTION

Carnegie Lecture Hall

Chairman: Edward Steidle

*The Rational Cleaning of Coal*

\*DR. R. LESSING, Consulting Chemist and Chemical Engineer, London  
Read by A. C. Fieldner

*Coal Cleaning Problems of Today*

DR. KARL GLINZ, Professor, Technische Hochschule, Berlin

*Gas Purification in Relation to Coal Sulphur*

F. W. SPERR, JR., Director of Research, The Koppers Company, Pittsburgh

Discussion and questions

## PULVERIZED FUEL SECTION

Carnegie Union, Carnegie Institute of Technology

Chairman: Harry L. Gandy

*Marine Use of Pulverized Fuel*

C. J. JEFFERSON, Head of the Fuel Conservation Section, United States Shipping Board, New York

COMMANDER J. J. BROSEK, Officer-in-charge, Fuel Oil Testing Plant, United States Navy, Philadelphia

*Characteristics and Properties of Fuels in U. S. S. R.*

\*PROFESSOR L. K. RAMZIN, Director of the Thermotechnical Institute, Moscow

Read by Dr. V. N. Krivobok, Carnegie Institute of Technology.

*Transportation of Pulverized Coal*

\*DR. ING. I. P. GOOSENS, Consulting Engineer, Aachen

Read by Professor T. G. Estep

Discussion

ERNEST H. PEABODY, Peabody Engineering Corporation, New York

## FERTILIZER SECTION

Faculty Club Room, Carnegie Institute of Technology

Chairman: Frank Whitmore

*The Mont Ceniz Process of Production of Synthetic Ammonia*

\*RUDOLF BATTIG, General Direktor, The Mont Ceniz Process, Westphalia

Read by Professor Willibald Trinks, Carnegie Institute of Technology

\*Indicates author is not present.

*The Processes of Georges Claude for the Separation of Gas by Liquefaction and the Synthesis of Ammonia*

JEAN DELORME, Director of the Ammonia Department, L'Air Liquide, Paris

Discussion and questions

AFTERNOON SESSIONS—2:30

LOW TEMPERATURE DISTILLATION SECTION

Carnegie Music Hall

Chairman: Charles L. Reese

*The Conversion of Slack Coal and Fines into Lumpy Smokeless Fuel—Low Temperature Coking—by the C. T. G. Process*

JOSEF PLASSMANN, Director, Chemisch-Technische Gesellschaft, Duisburg

Read by Hans Sieg, Berlin

*Low Temperature Distillation of Briquettes by Superheated Steam*

\*PAUL WEISS, Ingenieur-conseil des Mines de Vicoigne, Noeux et Drocourt, Paris

Read by Jacques Weiss, Ancien Elève de l'Ecole Polytechnique, Paris

*The Turner Retort*

CHARLES TURNER, Glasgow, Scotland

Discussions and questions

POWER AND COMBUSTION SECTION

Carnegie Union, Carnegie Institute of Technology

Chairman: Calvin W. Rice

*A New Method for the Determination of Melting Processes in Ash*

DR. KARL BUNTE, Professor, Technische Hochschule, Karlsruhe

*Removal of Ash and Loss of Carbon from Boiler Furnaces*

DR. DAVID S. JACOBUS, Advisory Engineer, Babcock and Wilcox Company, New York

E. G. BAILEY, President, Fuller Lehigh Company, Fullerton, Pennsylvania

*Clinkering of Coal Ash in Boiler Furnaces*

THOMAS G. ESTEP, Associate Professor, Mechanical Engineering, Carnegie Institute of Technology

Discussion and questions

LIQUEFACTION SECTION

Faculty Club Room, Carnegie Institute of Technology

Chairman: R. T. Haslam

*Some Aspects of the Hydrogenation of Coal*

J. IVON GRAHAM, Assistant Director, Mining Research Laboratory, University of Birmingham, Birmingham, England

\*Indicates author is not present.

*A New Method for the Determination of the Best Temperature for the Hydrogenation of Coals*

DR. J. P. AREND, Directeur des Société Arbed et Terres Rouges, Luxembourg

*Hydrogenation of Tar and Asphalt*

\*G. HUGEL, Professor, Ecole Nationale Supérieure du Pétrole et des Combustibles Liquides, Strasbourg

Read by W. E. Mott, Carnegie Institute of Technology

Discussions and questions

WEDNESDAY EVENING—8:15

Smoker, Gymnasium of the Carnegie Institute of Technology

## THURSDAY, NOVEMBER 22

MORNING SESSIONS—9:30

### GENERAL SESSION

Carnegie Music Hall

Chairman: Charles Camsell

*A Statement by* ARMANDO ROA, *Delegate from the Cuban Government*

*A Chemical Engineering View of Coal Processing*

DR. H. C. PARMELEE, Editor, "Chemical & Metallurgical Engineering," New York

*Some Factors for Consideration in an Appraisal of the Oil Possibilities of the United States*

DR. DAVID WHITE, Principal Geologist, U. S. Geological Survey, Washington

*Analysis of the Consumption of Coal in the United States*

F. G. TRYON, Washington

Discussions and questions

### PURIFICATION AND CLEANING SECTION

Carnegie Lecture Hall

Chairman: Arthur Neale

*Theory on Washing—Wet or Air Cleaning, Rhéolaveur or Jig*

A. FRANCE, Compagnie Internationale des Rhéolaveurs, Liège, Belgium

Read by J. R. Campbell, Scottdale, Pa.

*Interpretation of Float and Sink Data*

BYRON M. BIRD, Supervising Engineer, Southern Experiment Station, U. S. Bureau of Mines, Birmingham, Alabama

*Factors in Design of Coal Cleaning Plants*

JAMES B. MORROW, Research Engineer, The Pittsburgh Coal Company, Pittsburgh

Discussion and questions

\*Indicates author is not present.

## POWER AND COMBUSTION SECTION

Carnegie Union, Carnegie Institute of Technology

Chairman: John A. Hunter

*Fusing Point of Ash on Mixtures of Coal and Foreign Materials*

W. D. LANGTRY, President, Commercial Testing & Engineering Company, Chicago

J. H. KOHOUT, Chemical Director, Commercial Testing & Engineering Company, Chicago

*Coke Burning Domestic Boiler*

DR. CHARLES BRABBÉE, Director, Institute of Thermal Research, American Radiator Co., New York

*Boiler Furnaces for Bituminous Coal*

\*A. G. CHRISTIE, Professor of Mechanical Engineering, The Johns Hopkins University

Read by Professor W. Huff

*The Kilowatt Hour and Thermal Economy of Its Production*

A. R. SMITH, Engineer, Construction Engineering Department, General Electric Company, Schenectady

Discussion

HORACE C. PORTER, Consulting Chemical Engineer, Philadelphia

## LIQUEFACTION SECTION

Faculty Club Room, Carnegie Institute of Technology

Chairman: William J. Hale

*A Contribution to the Study of the Synthesis of Methyl Alcohol*

\*E. AUDIBERT, Directeur de la Société Nationale de Recherches sur le Traitement des Combustibles, Senlis, France

Read by Jean Bing

*Hydrogenation at High Pressure and High Temperature with or without Catalyzing Agents*

\*ANDRÉ KLING, Director, Laboratoire Municipal de la Ville de Paris

\*DANIEL FLORENTIN, Chemical Engineer and Assistant Director, Laboratoire

Municipal de la Ville de Paris

Read by Professor James Aston, Carnegie Institute of Technology

Discussion and questions

AFTERNOON SESSIONS—2:30

## LOW TEMPERATURE DISTILLATION SECTION

Carnegie Music Hall

Chairman: Maurice Holland

*Low Temperature Distillation of Coal by the Carbocite Process*

W. H. ALLEN, JR., Chemical Engineer, American Gas & Electric Company, New York

\*Indicates author is not present.

*Coal—The “L & N” Process*

\*HARALD NIELSEN, Consulting Engineer, “L & N” Coal Distillation, Ltd.,  
London

Read by Robert M. Crawford

*Low Temperature Distillation, The British Coal Industry and Oil Supplies*

\*R. H. CROZIER, Manager, Mineral Oils Extraction, Ltd., London

Read by W. E. Mott

Discussion and questions

**PURIFICATION AND CLEANING SECTION**

Carnegie Lecture Hall

Chairman: George H. Ashley

*Co-operative Control of Coal Purchases by Gas Works*

P. E. RAASCHOU, Professor in Technical Chemistry, The Royal Polytechnical  
College, Copenhagen

*The Reasons for the Need of Clean Coal*

\*F. R. WADLEIGH, Consulting Fuels Engineer, Consolidated Gas Company  
of New York, New York

Read by Dr. T. R. Alexander, Jr.

*The Sand Flotation Process*

THOMAS M. CHANCE, Consulting Mining Engineer, Philadelphia

*The Choice of a Coal Cleaning Plant*

GODFREY M. S. TAIT, Consulting Engineer, Washington

Discussion and questions

**POWER AND COMBUSTION SECTION**

Carnegie Union, Carnegie Institute of Technology

Chairman: Fred R. Low

*Locomotive Fuel*

W. L. ROBINSON, Superintendent, Fuel and Locomotive Performance,  
Baltimore and Ohio Railroad, Baltimore

*Carbonized Fuel—How will it be burned*

\*M. ALPERN, President, American Engineering Company, Philadelphia

Read by J. G. Worker, American Engineering Company, Philadelphia

*Black and White Coal in Austria*

DR. BARTEL GRANIGG, Mining University, Leoben, Austria

Discussion and questions

**TAR AND OIL SECTION**

Faculty Club Room, Carnegie Institute of Technology

Chairman: E. R. Weidlein

*Low Temperature Tars*

\*DR. A. MAILHE, Professor at the Sorbonne, Paris

Read by Jean Bing

\*Indicates author is not present.

*Continuous Distillation of Coal Tars and Crude Oils by Superheated Steam—  
The Abderhalden Process*

J. V. HENRI WINKLER, Director of the Research Department, Compagnie  
des Mines de Vicoigne, Noeux, et Drocourt, Paris

Discussion and questions

THURSDAY EVENING

Banquet, Hotel Schenley—6:30

**FRIDAY, NOVEMBER 23**

MORNING SESSIONS—9:30

**GAS SECTION**

Carnegie Lecture Hall

Chairman: W. H. Fulweiler

*Transmission of Coke Oven Gas in Pipe Lines in Germany*

\*DR. ALFRED POTT, General Direktor, Ruhrgas Aktiengesellschaft Essen  
Read by Dr. Wilhelm Roelen, Bergwerkdirektor, Vereinigte Stallwerke,  
A. G., Essen

*A Study of the Comparative Costs of Gas Production in the Retort House*

DR. E. W. SMITH, Technical Director, Woodall-Duckham Companies,  
London

*Gas and Tar Industries in France; Their Actual State and Their Tendencies*

JEAN BING, Comité Central des Producteurs et Distillateurs de Goudron  
en France, Paris

Discussion and questions

**LOW TEMPERATURE DISTILLATION SECTION**

Carnegie Union, Carnegie Institute of Technology

Chairman: M. C. Angloch

*Low Temperature Distillation of High Moisture Coals*

F. SEIDENSCHNUR, Professor, Staatliches Braunkohlenforschung-Institut  
der Bergakademie Freiberg

*Manufacturing Bituminous Coal from Petroleum*

DR. WALTER F. RITTMAN, Professor, Commercial Engineering, Carnegie  
Institute of Technology

*Low Temperature Carbonization of Coal by the Trumble Process*

COL. J. W. E. TAYLOR, Consulting Engineer, San Francisco

Discussion and questions

**TAR AND OIL SECTION**

Faculty Club Room, Carnegie Institute of Technology

Chairman: W. B. Plank

*Cracking of Tar Acids from Coal*

DR. J. C. MORRELL, Assistant Director of Research, Universal Oil Prod-  
ucts Company, Chicago

\* Indicates author is not present.

GUSTAV EGLOFF, Director of Research, Universal Oil Products Company, Chicago

*New Catalytic Processes for the Utilization of Coal Tar Crudes*

DR. ALPHONS O. JAEGER, Technical Director, The Selden Company, Pittsburgh

*A Process for the Catalytic Treatment of Hydrocarbons*

\*HENRI LAFOND, Compagnie Internationale pour la Fabrication des Essences et Pétroles, Paris

Read by Dr. T. R. Alexander, Jr.

Discussion and questions

#### AFTERNOON SESSIONS—2:30

### LOW TEMPERATURE DISTILLATION SECTION

Chairman: S. A. Taylor

*The "KSG" Low Temperature Carbonization Plant at New Brunswick, N. J.*

DR. R. P. SOULE, Chief Technologist, International Coal Carbonization Company, New York

*Principles of Briquetting, Coking and Noncoking Bituminous Coals*

EDGAR STANSFIELD, Professor of Research Chemistry, University of Alberta.

W. A. LANG, University of Alberta

*Transformation of Fine Bituminous Coal into Substitutes for Anthracite*

\*A. LÉAUTÉ, Société des Combustibles Purifiés, Paris

Read by Dr. T. R. Alexander, Jr.

Discussion and questions

### GAS SECTION

Carnegie Lecture Hall

Chairman: W. E. Fohl

*The Formation of Benzol and Other Hydrocarbons by the Action of Heat on Methane*

\*DR. FRANZ FISCHER, Kaiser Wilhelm Institut für Kohlenforschung, Mülheim-Ruhr, Germany

Read by Professor Walter F. Rittman, Carnegie Institute of Technology

*Low Temperature Phantom*

F. C. GREENE, The Old Ben Coal Corporation, Chicago

*Some Phases of the Organic Sulfur Problem in the Manufacture and Utilization of Gas*

WILBERT J. HUFF, Professor of Gas Engineering, Johns Hopkins University

Discussion and questions

\* Indicates author is not present.

### POWER AND COMBUSTION SECTION

Carnegie Union, Carnegie Institute of Technology

Chairman: Ambrose Diehl

*Pressure Electrolysis—Power and Fuel Oxyhydrogen in the Internal Combustion Motor*

DR. ING. J. E. NOEGGERATH, Berlin

*Some Potential Relations between Electricity and Coal Utilization*

A. T. STUART, Consulting Engineer, Toronto

*Fuel Tests and Plant Operation*

DR. ING. M. DOLCH, The Institute of Technical Chemistry of the University at Halle

Discussion

J. C. WARNER, Chemical Engineering Department, Carnegie Institute of Technology

### HIGH TEMPERATURE DISTILLATION SECTION

Faculty Club, Carnegie Institute of Technology

Chairman: S. P. Burke

*Fuel Problems in the Iron and Steel Industry*

EDGAR C. EVANS, National Federation of Iron & Steel Manufacturers and Honorary Secretary, Institute of Fuel, London

*Expenditure of Heat in the Coking Process*

DR. ING. ERNST TERRES, Direktor des Chem. Technischen Instituts der Technischen Hochschule, Braunschweig

*The Dry Quenching of Coke*

D. W. WILSON, Vice President, Dry Quenching Equipment Corporation, New York

Discussion

J. D. DAVIS, Bureau of Mines, Pittsburgh

### PUBLIC EVENING SESSION

8:15, Carnegie Music Hall

Chairman: Dr. Thomas S. Baker

*Some Thoughts of an Inventor on Scientific Research and Inventions*

GEORGES CLAUDE, Paris

## SATURDAY, NOVEMBER 24

MORNING SESSIONS—9:30

### GENERAL SESSION

Carnegie Music Hall

Chairman: George S. Davison

*The Part of the Catalyst in Coal Processing*

DR. HUGH S. TAYLOR, Professor of Chemistry, Princeton University

*Coal Problems in Perspective*

\*LORD MELCHETT, London

Read by Grant B. Shipley, Chairman and President, American Mond Nickel Company, Pittsburgh

*The Cracking of Low Temperature Coal Tars**The Berginization of Low Temperature Coal Tar in Presence of Catalysts*

DR. A. E. DUSTAN, Chief Chemist, Anglo-Persian Oil Company, London

*Research in the American Coal Industry*

HOWARD N. EAVENSON, Consulting Engineer, Pittsburgh

Discussion and questions

## GAS SECTION

Carnegie Lecture Hall

Chairman: W. S. Landis

*Producer Gas for Firing Boilers*

WILLIAM B. CHAPMAN, Consulting Engineer, New York

*Rational Utilization of Fuel Gases*†*Transportation of Industrial Gases*

\*C. SIMON, L'Administrateur Délégué, Société pour l'Exploitation des Tubes Electro-Frettés, Paris

Read by Jacques Weiss

*A Summary of Tests in Automobile Fuels*

\*A. GUISELIN, Secrétaire General, Commission Internationale Pétrole, Paris

Read by W. E. Mott

Discussion and questions

## LOW TEMPERATURE DISTILLATION SECTION

Carnegie Union, Carnegie Institute of Technology

Chairman: J. D. Davis

*Commercial Aspects of Low Temperature Coal Distillation and the International Bitumenoil Corporation Process*

J. A. VANDEGRIFT, Research Engineer, International Bitumenoil Corporation, New York

*Some Fundamentals of the Carbonization of Caking Coals; The Formation of Cenospheres*

\*F. S. SINNATT, Assistant Director, Fuel Research Board, London

Read by Edgar C. Evans

*Some New Aspects of the Economics of Coal*

\*DR. JACOBUS G. AARTS, Directeur Privaat Instituut voor Technologie, Dongen, The Netherlands

Read by Karl L. Kithil, Denver

Discussion and questions

\* Indicates author is not present.

†Read by title.

**HIGH TEMPERATURE DISTILLATION SECTION**

Faculty Club, Carnegie Institute of Technology

Chairman: Edward Steidle

*Progress Made in the Manufacture of Foundry Coke by the Pieters Continuous System of Coal Carbonization*

\*JULIEN PIETERS, Paris

Read by Dr. J. H. James

*Extraction and Recovery of Phenols from Ammonia Liquor*

ROBERT M. CRAWFORD, Chemical Engineer, Pittsburgh

Discussion and questions

**AFTERNOON SESSION**

Inspection Trip to the By-Product Coke Oven Plant at Clairton, Pennsylvania, of the Carnegie Steel Company. See Registration Desk for Details.

**RADIO TALKS**

Through the coöperation of KDKA, the local broadcasting station of the Westinghouse Electric and Manufacturing Co., a number of short speeches by speakers of the Carnegie Conference will be broadcast.

\* Indicates author is not present.

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*Note; This is a composite index of Volumes I and II; the italic numerals in parentheses indicate the volume. The names of authors of papers are set in capitals and small capitals, followed immediately by full titles of papers. (D) indicates participation in discussion of a paper.*

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